CAR. RY
OCT 28 1924

Volume XVIII October, 1924 Number 4

SOIL SCIENCE

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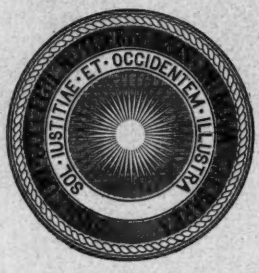
PUBLISHED MONTHLY
WILLIAMS & WILKINS COMPANY
MT. ROYAL AND GUILFORD AVENUES
Baltimore, Maryland, U. S. A.

Made in United States of America

SOIL SCIENCE



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THE DETERMINATION OF AMMONIA IN SOIL

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Received for publication November 30, 1923

Easily available nitrogen, particularly in the form of ammonia and nitrates, is one of the factors which most energetically accelerate the biological processes in the soil, e.g., the fermentation of cellulose (4). For soil biological research, therefore, it is of great importance to have methods by which these nitrogen compounds can be accurately determined. As for the nitrates, we have the exact phenol-disulfonic method. For ammonia, many methods have been proposed but some results obtained in this laboratory have indicated that the soil ammonia problem requires a reëxamination.

INTRODUCTION

Most of the soil nitrogen has its origin in the form of highly complex protein compounds. Under natural conditions these are decomposed very slowly and thereby amino acids and acid amids are gradually formed, which in their turn are hydrolyzed with the formation of ammonia. The ammonia nitrogen thus produced undergoes the further changes of the nitrogen cycle. One of the two big difficulties which arise when soil ammonia is to be determined is to establish this free ammonia without splitting off ammonia from the protein compounds or the intermediary compounds by the necessary chemical or physical operations.

Boussingault was probably the first to determine ammonia in soil. In order to avoid such hydrolysis he boiled the sample with the weak alkali MgO in water, fixed the liberated ammonia in sulfuric acid of known strength, and then determined the ammonia content by titration. However, it was found, especially with soils rich in humus, that the fresh distillate after continued treatment in this way reacts alkaline and that consequently ammonia is formed during the process. To avoid a quite arbitrary endpoint new methods were worked out. Schlösing modified the method of Boussingault in that he distilled a hydrochloric acid extract of the soil with MgO. Grandeau (11) as well as Baumann (5, 6) tested Schlösing's method and found it reliable. That nitrogen compounds can also be decomposed in Schlösing's method is indicated by the work of Berthelot and André (7). The azotometric method of Knop and Wolf (14) by which the soil is mixed with a solution of NaOH and NaOBr, whereupon the ammonia nitrogen is liberated as free nitrogen was rejected by Baumann because it gave ammonia figures to soils which were

free from ammonia according to Schlösing's method. Furthermore, strange contractions took place with the gasometric method which were difficult to eliminate. Valmari (25) tried to extract the ammonia with the neutral electrolytes NaCl, $CaCl_2$ and $CaCO_3$, after which the ammonia was determined on an aliquot of the filtered extract by distillation with MgO. From his results Valmari concluded that solutions of neutral electrolytes even in low concentrations remove all the soil ammonia, and that generally 0.1 *N* NaCl in the extracting ratio, that is, the ratio between soil and liquid, 1:40 or 1:20 will be suitable for peat soils, 0.2 *N* NaCl in the ratio 1:10 for peat loam soils, and 0.5 *N* NaCl in the ratio 1:2 for mineral soils.

In the study of all the related methods, they were controlled by continuing the process for such a period as was thought sufficient for complete ammonia liberation and by making blanks on organic nitrogen compounds such as amino acids, acid amids, and other nitrogenous organic compounds. In determining the efficiency of various methods, no one, it seems, with the exception of Knop and Wolf (14) tried to recover from the soil ammonia previously added in known amount in the form of ammonium salts.

During the last decennium control investigations of this kind have been taken up again by Potter and Snyder (21), McBeth (19), and others, who found that soils retain ammonia nitrogen supplied in the form of ammonia or ammonium salts so firmly that it cannot be recovered quantitatively by any one of the usual methods for the determination of ammonia in soil.

Since added ammonia could not be recovered by the old methods for the determination of soil ammonia, the problem has been treated again by several investigators, who have worked out new methods. The purpose of this work was to determine whether these new methods are generally applicable and also to find out how far certain factors influence the ammonia-fixing power of the soil. Then, guided by these results, it was hoped to find a new way to solve the problem.

It appears from the foregoing that the properties such a method should possess, besides being rapid and simple, are;

1. The ammonia nitrogen of the soil should be liberated quantitatively and none should be produced from organic nitrogen compounds during the work, even after the addition of such compounds.

2. In the case of a soil to which ammonia nitrogen has been added, the method must be able to recover this quantitatively together with the soil ammonia nitrogen.

That the fulfillment of point 2 is not a sufficient condition is illustrated by the following example from an investigation of this kind on manure (4). Boussingault's method as well as that of Baragiola and Schuppli (1) accounted quantitatively for added ammonia nitrogen, but the former method gave the higher total yield, due to liberation of more ammonia from the control. Thus Boussingault's method gave incorrect results for the material in question, but to determine whether the latter method really is correct it must be tested according to point 1.

The second condition being essential, the work first related was an attempt to find out how the different methods behaved with reference to soils to which ammonia nitrogen was added. Some of the results presented here have already been published (2, 3), but for the sake of completeness they are included.

The following soils were used in the experiments:

		pH
Soil	I. Silt loam soil from Experimentalfältet	5.7
Soil	II. Heavy clay soil from Experimentalfältet	7.1
Soil	III. Peat loam soil from Experimentalfältet	5.3
Soil	IV. Sandy soil from Risbyn, Avesta	5.0
Soil	V. Sandy soil from Experimentalfältet	6.1
Soil	VI. Loam soil from Experimentalfältet	5.5
Soil	VII. Peat loam soil from Vassbo, Ornäs	5.4

BOUSSINGAULT'S METHOD

McBeth found that the methods of Boussingault and Schlösing were very nearly of the same worth in the recovery of added ammonia. For the determinations of soil ammonia which have previously been made in this laboratory only the former of these methods were used. As a rule, those investigations had reference to soils relatively poor in humus for which, according to König (15), the Boussingault method gives approximately correct values. For the estimation of our earlier results it was, therefore, of interest to examine to what extent added ammonia nitrogen could be liberated from these soils by the Boussingault method. The determinations were made by heating 50 gm. of soil with about 5 gm. of MgO and 500 cc. of distilled water. A piece of bees' wax was added otprevent foaming. The liberated ammonia was caught in 0.1 *N* H_2SO_4. Three hundred cubic centimeters of distillate was taken since a preliminary experiment with soil II had shown that the part of the added ammonia which was removable was obtained in this volume. The distillates were boiled for a few minutes, after which they were titrated after cooling with 0.1 *N* NaOH, cochineal being used as the indicator. In those cases where the soil was supplied with ammonia nitrogen this was always added in the form of $(NH_4)_2SO_4$ solution in a volume of 25 cc. per 50 gm. of soil. This volume of liquid always proved to be sufficient to wet the whole sample thoroughly. After repeated shaking the mixture was allowed to stand 1 hour before examination.

A block of each soil was divided into layers with the depth limits 5 to 15 and 25 to 35 cm. from the soil surface. Each soil layer was then dried at room temperature, sifted and thoroughly mixed. This division into layers was made, because McBeth (19) found that the ammonia-fixing power of soil increases with the depth from which it has been taken, with the exception of peat soils which seemed to digress from this rule. The results of these experiments are shown in table 1. The data given are in all cases, here as well as in the following tables, the average of two closely agreeing values. The percentage of nitrogen loss is calculated on the quantity of nitrogen added.

The results obtained accord throughout with those of McBeth, even though the losses here are much smaller. Both of the mineral soils show an increased fixing power by the deeper layer with all concentrations of ammonia, while with the peat soil the result is the reverse of this. It must be pointed out,

TABLE 1

Results of experiments with Boussingault's method

NUMBER AND DEPTH OF THE SOIL SAMPLE	AMMONIA NITROGEN			
	Added per 50 gm. soil	Found	Lost	
	mgm.	*mgm.*	*mgm.*	*per cent*
Soil I; 5–15 cm.	0.00	2.24	....	.....
	10.75	12.60	0.39	3.63
	21.50	22.82	0.92	4.28
	32.26	33.60	0.90	2.79
	53.76	55.16	0.84	1.56
Soil I; 25–35 cm.	0.00	2.66	....	.....
	10.75	12.04	1.37	12.74
	21.50	22.26	1.90	8.84
	32.26	33.04	1.88	5.83
	53.76	53.62	2.80	5.21
Soil II; 5–15 cm.	0.00	3.50	....	.....
	10.75	12.32	1.93	17.95
	21.50	22.12	2.88	13.40
	32.26	31.92	3.84	11.90
	53.76	52.99	4.27	7.94
Soil II; 25–35 cm.	0.00	2.94	....	.....
	10.75	9.66	4.03	37.49
	21.50	18.06	6.38	29.67
	32.26	28.14	7.06	21.88
	53.76	47.95	8.75	16.28
Soil III; 5–15 cm.	0.00	7.28	....	.....
	52.64	57.12	2.73	5.19
Soil III; 25–35 cm.	0.00	2.66	....	.....
	52.64	53.34	1.96	3.72

however, that the last-mentioned soil was hardly of peat character at the lower depth.

In this connection it is noted that Münter (20) has made comparative investigations between the original form of the Boussingault method, and also of a modified form, by which the distillation was made first after the addition of a neutral salt, e.g., KCl. With zeolites this procedure proved to be effective.

On the contrary, the added ammonia nitrogen could not be recovered from heavy clay soils either with MgO alone or after addition of KCl. The last-mentioned result was confirmed here by investigations on soil II.

THE METHOD OF BARAGIOLA AND SCHUPPLI

The Boussingault method being defective, that of Baragiola and Schuppli (1) was tried. According to the authors this method will solve both phases of the problem.

TABLE 2

Results of experiments with the method of Baragiola and Schuppli

NUMBER AND DEPTH OF THE SOIL SAMPLE	AMMONIA NITROGEN							
	Baragiola and Schuppli's method				Boussingault's method			
	Added per 50 gm. soil	Found	Lost		Added per 50 gm. soil	Found	Lost	
	mgm.	*mgm.*	*mgm.*	*per cent*	*mgm.*	*mgm.*	*mgm.*	*per cent*
Soil I; 5–15 cm.	0.00	0.21	.....	.....	0.00	2.24	....	....
	54.15	51.17	3.19	5.89	53.76	55.16	0.84	1.56
Soil II; 5–15 cm.	0.00	0.07	.....	.....	0.00	3.50	....	....
	54.15	46.62	7.60	14.04	53.76	52.99	4.27	7.94
Soil II; 25–35 cm.	0.00	1.89	.....	.....	0.00	2.94	....	....
	54.15	40.81	15.23	28.13	53.76	47.95	8.75	16.28
Soil III; 5–15 cm.	0.00	0.07	.....	.....	0.00	7.28	.....	.....
	54.15	52.29	1.93	3.56	52.64	57.12	2.73	5.19
Soil II; 5–15 cm. (sterilized)	0.00	0.91	.....	.....	0.00	3.50	.....	.....
Soil III; 5–15 cm. (sterilized)	0.00	6.30	.....	.....	0.00	9.38	....	.....

In these experiments it was necessary to use a vacuum of 30 to 40 mm. because of the low water pressure. Because of this, the bath temperature was increased to about 40°C. but even then the distillation required a time of 3 to 4 hours. Further alterations were made in that the receiving flask contained 0.1 *N* H_2SO_4, and that cochineal was used instead of congo red. The ammonia nitrogen was supplied as previously described in the form of an $(NH_4)_2SO_4$ solution. These results together with those of the Boussingault method are shown in table 2.

The values obtained by the vacuum method for the blank soils are remarkably low. This accords very well with the results obtained by Baragiola and Schuppli, for as a rule they found the soils to be ammonia-free. Only the last two soils, sterilized in an autoclave at 120°C. for 1½ hours, show ammonia

figures which approach those of the parallel method. This indicates that ammonia was split off from organic nitrogen compounds when the determination was made by the Boussingault method. It is impossible to determine whether the figures obtained for the blank soils by the vacuum method are correct, as this method has been able to liberate the nitrogen added in less degree than the Boussingault method.

THE STEINKOPF METHOD

Some experiments were made also with the Steinkopf (23) vacuum distillation method. This method has not been presented with the present object in view, but it naturally seemed to be adapted for this purpose. The apparatus of Baragiola and Schuppli was used. As before, 5 gm. of MgO and 100 cc. of water were added to 50 gm. of soil. The pressure was about 40 mm. and

TABLE 3

Results of experiments with Steinkopf's method

AMMONIA NITROGEN ADDED PER 50 GM. SOIL	AMMONIA NITROGEN								
	Steinkopf's method			Baragiola and Schuppli's method			Boussingault's method		
	Found	Lost		Found	Lost		Found	Lost	
mgm.	*mgm.*	*mgm.*	*per cent*	*mgm.*	*mgm.*	*per cent*	*mgm.*	*mgm.*	*per cent*
0.00	0.14	....	.....	1.89	.....	.....	.....	....	....
54.15	42.20	8.09	14.94	40.81	15.23	28.13	.....	....	.....
0.00	0.14	....	.....	0.07	.....	.....	2.24	....	....
53.76	50.82	3.08*	5.73	44.59	9.24	17.19	51.66	4.34	8.07

*After the first distillate taken the loss was 6.30 mgm., or 11.72 per cent.

the bath temperature 40°C. The ammonia-free steam was led in through the capillary tube prescribed in the former method. With the first two samples (soil II from 25 to 35 cm.) the distillation was discontinued when the distillate had reached 450 cc.; with the last two (soil II from 0 to 20 cm.), two similar distillates were caught. The results of the experiment are brought together in table 3, where the values obtained by the first vacuum method and the Boussingault method also are shown.

The results show that Steinkopf's method, like the first vacuum method, gives very low ammonia figures for the blank soils. When nitrogen was added, this was liberated most effectively by Steinkopf's method but the yield was not quantitative even when the volume of distillate amounted to 900 cc.

THE POTTER AND SNYDER METHOD

As mentioned before Potter and Snyder among others have shown that the older methods for determination of soil ammonia are incorrect. In this connection they work out a new procedure (21).

As the speed of aeration could not be brought to more than 200 liters per hour in these experiments, the time of treatment was increased to 20 hours. The ammonia nitrogen was supplied as previously described. The results in table 4 show that this method has given about the same result as the two vacuum methods.

MATTHEWS' METHOD

The method by Matthews (18) is based on the same principle as the former method. Matthews, however, uses an apparatus which makes it possible to give an exceedingly thorough treatment to the whole sample during the analysis, whereas in the Potter and Snyder method, at least as it was carried

TABLE 4

Results of experiments with Potter and Snyder's method

NUMBER AND DEPTH OF THE SOIL SAMPLE	AMMONIA NITROGEN ADDED PER 25 GM. SOIL	AMMONIA NITROGEN					
		Potter and Snyders's method			Boussingault's method		
		Found	Lost		Found	Lost	
	mgm.	*mgm.*	*mgm.*	*per cent*	*mgm.*	*mgm.*	*per cent*
Soil II; 5–15 cm.	0.00	0.07	....	.....	1.82	....	.....
	21.53	17.43*	4.17	19.37	22.40	0.95	4.41
Soil II; 15–25 cm.	0.00	0.00	....	.....	3.29	....	.....
	21.53	17.82	3.71	17.23	22.26	2.56	11.89
Soil II; 25–35 cm.	0.00	0.00	....	.....	1.37	....	.....
	27.02	20.41	6.61	24.46	22.89	5.50	20.36

*In one of the two parallel trials the receiver was exchanged after 20 hours and the aeration continued for 20 hours more. The loss then decreased to 1.86 mgm., or 8.64 per cent.

out here, it sometimes happens that a part of the sample stays at the bottom of the flask and thus possibly escapes from the effect of the air current.

As a rule, Matthews recovered added ammonia with an accuracy of 98 to 99.5 per cent in 6 hours, and with nearly equal accuracy in 3 hours, when the ammonia nitrogen was added in amounts corresponding to 5.55 and 11.1 mgm. per 100 gm. of soil. With calcareous soils, however, the losses were considerable. Unmanured field soils were found to keep 1.4 to 8.0 mgm. of ammonia nitrogen per kilogram.

In the experiments carried out with this method, Matthews' directions were followed accurately. The time of aeration was in no case shorter than 6 hours. The nitrogen was supplied as previously described. In two cases, noted in table 5, 0.1 *N* acid and 0.1 *N* alkali were used instead of the 0.02 *N* solutions in order to obtain the same degree of accuracy as in the former experiments. Moreover, one experiment was made by which Matthews'

alkaline solution was exchanged by a solution with equivalent amounts of potassium salts.

From table 5 it appears that Matthews' method is not generally applicable. It must be noted that soil II does not belong to that group of soils (calcareous soils) for which the method will give less correct results. This soil was of neutral reaction (pH = 7.1). The experiment with the sand soil (no. IV) has given an unsatisfactory result also. For the blank soils the method has yielded values comparable to those obtained by the vacuum methods and Potter and Snyder's method. In the experiment where Matthews' alkaline solution was exchanged for the corresponding potassium salt solution, the yield is about the same as with the original method.

TABLE 5

Results of experiments with Matthew's method

NUMBER AND DEPTH OF THE SOIL SAMPLE	AMMONIA NITROGEN				NOTES
	Added per 25 gm. soil	Found	Lost		
	mgm.	*mgm.*	*mgm.*	*per cent*	
Soil II; 0–20 cm	0.000	0.168	.....	.....	
	2.763	2.688	0.243	8.80	
	12.558	12.089	0.637	5.08	
	0.00	0.00	.....	....	0.1 *N* acid and alkali
	12.53	11.72	0.81	6.43	0.1 *N* acid and alkali
Soil II; 25–35 cm	0.00	0.07	.....	....	0.1 *N* acid and alkali
	12.60	11.17	1.51	11.95	0.1 *N* acid and alkali
Soil IV; 0–20 cm	0.000	0.168	.....	....	
	12.558	12.264	0.462	3.68	
Soil II; 0–20 cm	0.000	0.168	.....	....	Equivalent K solution
	12.558	11.928	0.798	6.35	Equivalent K solution

THE METHOD OF GIBBS, NEIDIG AND BATCHELOR

Recently Gibbs, Neidig and Batchelor (10) have modified Potter and Snyder's method, in an effort to decrease the time of aeration. They worked with a neutral silt loam soil and succeeded in recovering the nitrogen quantitatively from samples supplied with $(NH_4)_2SO_4$ in an amount corresponding to 43 mgm. of nitrogen per 100 gm. of soil. Their results showed also that nitrogenous organic soil compounds are not split by this method.

The experiments with the addition of $(NH_4)_2SO_4$ have been repeated here following the directions given. After aeration during $1\frac{1}{2}$ hours a new receiving flask was attached and the treatment continued for $1\frac{1}{2}$ hours more.

Table 6 shows that in none of the cases examined has the added nitrogen been recovered quantitatively. That part of it which can be liberated is present in the first distillate. A prolongation of the time of treatment causes a considerable increase of the ammonia figures of the blank samples from which it is evident that organic nitrogen compounds of the soils were attacked.

EXPERIMENTS WITH DIFFERENT EXTRACTING AGENTS

The direct methods having shown their imperfection some further experiments were made on extracting the ammonia nitrogen. Soil II (in the layer from 0 to 20 cm.) was used because it was previously found to be the strongest binder of ammonia. Of the samples supplied with ammonia nitrogen, in each case 50 cc. of $(NH_4)_2SO_4$ solution was added to 100 gm. of soil and this mix-

TABLE 6

Results of experiments with the method of Gibbs, Neidig and Batchelor

NUMBER AND DEPTH OF THE SOIL SAMPLE	AMMONIA NITROGEN ADDED PER 100 GM. SOIL	AMMONIA NITROGEN					
		1½ hours' aeration			3 hours' aeration		
		Found	Lost		Found	Lost	
	mgm.	*mgm.*	*mgm.*	*per cent*	*mgm.*	*mgm.*	*per cent*
Soil II; 15–25 cm.	0.00	1.61	.....	.....	3.15	.....	.....
	49.77	47.65	3.73	7.49	49.23	3.69	7.41
Soil II; 25–35 cm.	0.00	0.98	.....	.....	1.47	.....	.....
	49.77	39.76	10.99	22.08	41.02	10.22	20.53
Soil III; 5–15 cm.	0.00	2.03	.....	.....	3.50	.....	.....
	49.77	44.55	7.25	14.57	47.35	5.92	11.89

ture was then shaken repeatedly for 1 hour in a stoppered flask. According to the literature this time is sufficient for the equilibrium between the soil and a solution of an ammonium salt to reach a point very close to the final state of equilibrium. Then 150 cc. of a solution of the various compounds indicated was added in such strength that the concentration after dilution by the liquid already present became that given in the table. The soil water (18.16 per cent), however, was not included here, but was considered in the calculations. When the extracting agents had been added, the mixture was allowed to stand 24 hours as before. The ammonia was then determined by distilling 100 cc. of the filtered extract with an excess of MgO.

The efficiency of the extracting agents of Schlösing and Valmari (0.5 *N* HCl and 0.5 *N* NaCl), respectively, as compared with that of water was first determined.

The results in table 7 show that the method of Schlösing, and much less that of Valmari, have not been able to recover the nitrogen added. Compared

with water, the extracting agent of Schlösing has shown the much greater extracting effect as to the nitrogen added, while the salt solution of Valmari

TABLE 7

Results of experiments with the extracting agents of Schlösing and Valmari

EXTRACTING AGENTS	AMMONIA NITROGEN			
	Added per 100 gm. soil	Found	Lost	
	mgm.	*mgm.*	*mgm.*	*per cent*
Water	0.00	0.00	.....	.....
	49.28	14.66	34.62	70.25
0.5 *N* HCl	0.00	0.84	.....	.....
	50.47	41.54	9.77	19.36
0.5 *N* NaCl	0.00	0.15	.....	.....
	49.28	27.04	22.39	45.44

TABLE 8

Results of experiments with $CaCl_2$ as the extracting agent

EXTRACTING AGENTS	AMMONIA NITROGEN			
	Added per 100 gm. soil	Found	Lost	
	mgm.	*mgm.*	*mgm.*	*per cent*
0.5 *N* $CaCl_2$	0.40*	0.15	0.25	.....
	49.68	32.08	17.60	35.43
1 *N* $CaCl_2$	0.80*	0.61	0.19	.....
	50.08	36.96	13.12	26.20
2 *N* $CaCl_2$	1.61*	1.68	−0.07	.....
	50.89	40.77	10.12	19.89
4 *N* $CaCl_2$	3.22*	2.75	0.47	.....
	52.50	43.52	8.98	17.10
0.5 *N* HCl	0.00	0.84	.....	.....
	50.47	41.54	9.77	19.36
0.5 *N* HCl plus 0.5 *N* $CaCl_2$	0.40*	1.15	0.09	.....
	50.87	43.68	8.03	15.79
0.5 *N* HCl plus 1 *N* $CaCl_2$	0.80*	1.30	0.34	.....
	51.27	43.63	8.48	16.54

*Present in the $CaCl_2$ solution.

has been rather unimportant. It appears from a later paper by Valmari (26) that he himself has discovered this defect in his method.

A water extract of this present soil contains only a trace of soluble Ca compounds, but after treatment of the soil with $(NH_4)_2SO_4$ solution the test for Ca is unmistakable. Because of this it was determined to see if an addition of soluble Ca salts would increase the liberation of the ammonia. The $CaCl_2$

TABLE 9

Results of experiments with potassium and aluminum salts as extracting agents

EXTRACTING AGENTS	pH OF THE EXTRACTS	AMMONIA NITROGEN			
		Added per 100 gm. soil	Found	Lost	
		mgm.	*mgm.*	*mgm.*	*per cent*
1 *N* KCl	7.0	0.00	0.00	.....	.....
	7.0	50.12	44.48	5.64	11.26
0.5 *N* KH_2PO_4	5.1	0.00	0.15	.....	.....
	5.1	50.12	35.12	15.15	30.23
1 *N* KCl plus 0.5 *N* KH_2PO_4	5.0	0.00	0.15	.....	.....
	5.0	50.12	45.11	5.16	10.30
1 *N* KCl plus 1.6 gm. $KHSO_4$	4.6	0.00	0.54	.....	.....
	4.6	50.12	45.54	5.12	10.22
1 *N* $Al_2(SO_4)_3$	3.6	2.24*	1.22	1.02	.....
	3.6	52.36	38.23	14.13	26.99

*Added with the aluminum salt.

TABLE 10

Results of experiments with methyl and ethyl alcohol as extracting agents

EXTRACTING AGENTS	AMMONIA NITROGEN			
	Added per 100 gm. soil*	Found	Lost	
	mgm.	*mgm.*	*mgm.*	*per cent*
10 per cent methyl alcohol	0.00	0.00	.....	.....
	50.26	14.62	35.64	70.91
10 per cent ethyl alcohol	0.00	0.46	.....	.....
	50.26	14.70	36.02	71.67
70 per cent ethyl alcohol	0.00	0.00	.....	.....
	50.26	0.92	49.34	98.17

preparation used in this experiment was not free from ammonia, as indicated in the following table. The experiment was completed by an investigation upon the combined effect of $CaCl_2$ and HCl. The results of the experiment appear in table 8. The former results from the extraction with 0.5 *N* HCl

have been included. The losses obtained after treatment with 0.5 *N* HCl plus $CaCl_2$ solution have been calculated on the soil ammonia figure of the Schlösing method as standard.

It was thought that the results from some experiments by Cook (9) and McBeth (19) might indicate more effective extracting agents. Cook determined the ammonia adsorption by treating 50 gm. of soil with 200 cc. of 0.01 *N* $(NH_4)_2SO_4$, after which the amount of ammonia unfixed was obtained by distilling an aliquot of the filtered extract with NaOH. When he added small amounts of K_2SO_4, KCl or acid phosphate to the soil before the addition of the $(NH_4)_2SO_4$ solution, as a rule he found a distinct decrease of the adsorption of ammonia. McBeth, extracting his soils with HCl according to Schlösing, found for one soil by supplying 10 cc. of 1 *N* $Al_2(SO_4)_3$, $AlCl_3$, or $Al(NO_3)_3$ to 100 gm. of soil 30 minutes before the addition of $(NH_4)_2SO_4$ (50 mgm. of *N*), that the amount of ammonia retained was reduced from 47 to about 11 per cent. When he exchanged the Al salts with the equivalent amounts of K salts for the same soil this amount of ammonia was brought down to about 6 per cent.

With these results in mind the following experiments, the data of which are given in table 9, were made. The combination of 1 *N* KCl with 1.6 gm. of $KHSO_4$ was undertaken since a preliminary experiment had shown that this amount of $KHSO_4$ gave a lower pH value to the extract than did 1 *N* KCl plus 0.5 *N* KH_2PO_4. The pH values were determined colorimetrically on the filtered soil extracts. The aluminum sulfate employed was not free from ammonia.

Compared with pure water (table 7) all these extracting agents have liberated considerably more of the nitrogen added. This is especially true where KCl was used either alone or together with KH_2PO_4 or $KHSO_4$. Naturally this is allied to the special position of the K and NH_4 ions in adsorption in the soil, which is opposite to that of the other cations. $Al_2(SO_4)_3$ was found to be much less effective than in McBeth's experiments. The results shown in table 9 indicate that an increase of the hydrogen-ion concentration of the extract cannot play any important part in the liberation of ammonia from this neutral soil. This fact will be still more obvious if the pH value obtained in the extraction according to Schlösing also is considered. This pH determination, performed by Biilmann's quinhydrone method (8), gave the result pH = 0.5. At the same time (table 7) a considerably smaller amount of ammonia was recovered than by extraction with KCl.

All the former extracting agents except the hydrochloric acid have a greater surface tension than the water, and, as the hydrochloric acid sets free a strong concentration of salts from the soil, the result in this case also is an extracting agent of the same kind. As it was thought of interest to find out how solutions of a smaller surface tension than that of water acted, the experiments reported in table 10 were made.

Both the 10 per cent solutions have given the same result as pure water (table 7). The concentrated ethyl alcohol has removed only 0.92 mgm. of the nitrogen added, corresponding to 4.34 mgm. of $(NH_4)_2SO_4$, while the volume of liquid used should have been able to dissolve about 680 mgm. of this salt.

EXPERIMENTS WITH REPEATED SUCCESSIVE EXTRACTIONS

Experiments to leach added ammonia with water have shown that a quantitative recovering in this way is not to be expected. Cook (9) tried two methods of procedure for determination of the adsorbing power of the soil. That method which was used in his later investigations has been previously described. The second method was as follows: 50 gm. of soil were placed on a filter and then 8 cc. of 1 *N* $(NH_4)_2SO_4$ was added. The soil was brought to optimum moisture and allowed to stand for 4 hours, after which it was leached with water. The successive 200-cc. portions of the filtrate were then analyzed for ammonia. Cook found that practically all the ammonia nitrogen which could be extracted in this way was present in the first portion. McBeth (19), who added 50 mgm. of ammonia nitrogen per 100 gm. of soil found for one of the soils examined by leaching with water, that 23 per cent of this nitrogen was present in the first 400-cc. portion and after collecting six similar portions the yield had risen to 33 per cent. When the same soil was leached with hydrochloric acid, the corresponding figures were 52 and 81 per cent. The above results did not encourage the use of water or hydrochloric acid in leaching experiments. However, it might be expected that a potassium salt solution would be more suitable for this purpose, partly because of McBeth's results after addition of K salts and partly because of the experiments previously described in which the KCl solution was found to be the most effective agent. Some experiments by Kellner may be interpreted in favour of this assumption. Having found that the soil adsorbs the K and NH_4 ions in equivalent amounts (12), he worked out a method (13), for the determination of assimilable potassium of the soil, by which the potassium was extracted successively with a hot NH_4Cl solution. If this procedure is of general application it might be possible to liberate all the soil ammonia by inverting the method, that is by exchanging NH_4Cl for KCl. For this, however, one needs to work at room temperature or lower. McBeth (19) found for one soil that the amount of ammonia fixed rose from 45 to 65 per cent when the temperature of the soil was increased from 5 to 100°C. For another soil these percentages were 75 and 87 respectively. That high temperatures are not necessary is a fortunate circumstance, for with an increase in temperature there is a greater risk of splitting off ammonia from the organic nitrogen compounds of the soil.

For the next experiment Kellner's method consequently was altered to the following procedure: 25 gm. of soil was placed in a beaker and 12.5 cc. of $(NH_4)_2SO_4$ solution added. The mixture was repeatedly stirred for 1 hour.

Then 50 cc. of 3.5 *N* KCl solution was added, the contents of the beaker were stirred from time to time and then allowed to settle, and after ½ hour in all the solution was decanted to a filter which held exactly 50 cc. Again 50 cc. of the KCl solution was added to the residue in the beaker and the treatment was repeated until 20 filtrates had been secured. Two ammonia determinations were made on each sample; the first ten filtrates being combined for one determination and the following ten filtrates combined for the other determination. The determinations were made by distilling with MgO, the ammonia liberated being caught in 0.02 *N* H_2SO_4, which afterwards was titrated with 0.02 *N* NaOH, methyl red being used as the indicator. Each filtrate was tested for ammonia with Nessler's reagent. As the successive filtrates from the blank sample also showed a strong ammonia reaction, the KCl solution (prepared with Kahlbaum's KCl "Zur Analyse") was examined with the same

TABLE 11

Results of a preliminary experiment in inversion of Kellner's method

AMMONIA NITROGEN ADDED PER 100 GM. SOIL*	AMMONIA NITROGEN			
	Extracts 1–10		Extracts 11–20	
	Found	Lost	Found	Lost
mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*
0.000	1.414	0.335	1.554	0.195
12.530	13.090	1.189	1.540	0.209

* The nitrogen of the KCl solution not included.

reagent and it was then found to contain ammonia. A quantitative determination found 1.749 mgm. of ammonia nitrogen per 500 cc. of the KCl solution. The experiment is recorded in table 11.

It is evident that this experiment does not indicate the adaptability of the procedure for the purpose in question. In fact, the soil had been treated uninterruptedly with a dilute solution of ammonia. Since the definite equilibrium between the soil and this solution has been maintained, the latter will leave the soil with an unaltered concentration of NH_4. This also may be seen from the experiment.

In order to obtain a better idea of the last method the work was continued with ammonia-free KCl solution, prepared by boiling a concentrated solution of KCl and KOH until the ammonia was driven off, after which the solution was neutralized with ammonia-free HCl. As the 3.5 *N* KCl leaves a troublesome salt crust on the filter, some comparative experiments were made with 3.5 and 0.5 *N* KCl, and it was found that the weak solution was quite as available as the stronger one by this procedure. Because of this the extractions in the later experiments were carried out with 0.5 *N* KCl. It was also evident that the use of 0.02 *N* H_2SO_4 and 0.02 *N* NaOH meant a superfluous refinement of the method, so these solutions were exchanged for the 0.1 *N*

solutions. In order to decrease the experimental error all the filtrates were collected in the same Florence flask, which, after addition of MgO, was attached to the distilling apparatus. Only in those cases where twenty or still more filtrates were caught the ammonia determination was made on an aliquot of the combined filtrates. The samples with $(NH_4)_2SO_4$ added were extracted in this way until the filtrate no longer gave a coloration with Nessler's

TABLE 12

Results of experiments on different mineral soils with successive extractions with 0.5 N KCl

NUMBER AND DEPTH OF THE SOIL SAMPLE	SOIL	NUMBER OF EXTRACTIONS	AMMONIA NITROGEN			
			Added per 25 gm. soil	Found	Lost	
			mgm.	*mgm.*	*mgm.*	*per cent*
Soil I; 0–20 cm	Silt loam	12	0.00	0.14	.....	.....
		12	12.64	12.46	0.32	2.53
Soil II; 5–15 cm	Heavy clay	15	0.00	0.00	.....	.....
		15	12.04	12.15	−0.11	−0.87
Soil II; 0–20 cm	Heavy clay	15	0.0	0.07	.....	.....
		15	12.64	12.35	0.36	2.81
Soil II; 15–25 cm	Heavy clay	15	0.00	0.25	.....	.....
		15	12.60	12.32	0.53	4.21
Soil II; 25–35 cm	Heavy clay	15	0.00	0.14	.....	.....
		15	12.04	10.33	1.85	15.44
Soil IV; 0–20 cm	Sand	10	0.00	0.04	.....	.....
		10	12.57	12.56	0.05	0.36
Soil V; 0–20 cm	Sand	10	0.00	0.42	.....	.....
		10	12.60	12.92	0.10	0.83
Soil VI; 0–20 cm	Loam	10	0.00	0.00	.....	.....
		10	12.64	12.74	−0.10	−0.79

reagent, and for the sake of uniformity the same number of extractions were performed on the blank samples.

In table 12 a number of experiments on mineral soils, carried out by this new procedure, are brought together.

It appears from table 12 that the procedure here used must be considered quite satisfactory in the case of surface soils, or those taken from the depth of 0 to 20 cm. However, it did not succeed in recovering all the added ammonia from the lower layers of the heavy clay soil. Other experiments made with this soil are reported later.

No long period of time should elapse between the successive extractions. If, for example, the soil suspension is set aside until the following day a distinct ammonification sets in. This, however, can be prevented by the addition of 1 to 5 gm. of $HgCl_2$ to each liter of 0.5 *N* KCl. Special experiments showed that such an addition of $HgCl_2$ will not influence the extracting power of the solution. In these instances the ammonia distillations were of course made after the mercury was precipitated as HgS. The use of this last extracting agent has the disadvantage that the extracting process cannot be followed with Nessler's reagent, because of the brown precipitate which is formed by Nessler's solution in the presence of $HgCl_2$.

TABLE 13

Results of experiments on peat loam soils with successive extractions with 0.5 N KCl

NUMBER AND DEPTH OF THE SOIL SAMPLE	AMMONIA NITROGEN			
	Added per 25 gm. soil	Found	Lost	
	mgm.	*mgm.*	*mgm.*	*per cent*
Soil III; 5–15 cm	0.00	0.00	.....	.....
	12.04	12.01	0.03	0.29
Soil VII; 0–20 cm	0.00	0.07	.....	.....
	12.57	12.67	−0.03	−0.24

TABLE 14

Results of experiments to determine the effect of lime upon extraction

ADDITIONS PER 25 GM. SOIL		AMMONIA NITROGEN			NOTE
$CaCO_3$	NH_4-N	Found	Lost		
gm.	*mgm.*	*mgm.*	*mgm.*	*per cent*	
0.0	0.00	0.04	....	....	
2.0	12.57	12.36	0.25	2.03	
2.0	12.57	12.53	0.08	0.64	The first extraction with HCl

In the case of peat soils where there is much material which will not settle, the following procedure was used: 25 gm. of soil was placed on a hardened filtered in a Büchner funnel fixed to a suction flask, and 12.5 cc. of a solution of $(NH_4)_2SO_4$ added. After 1 hour 50 cc. of 0.5 *N* KCl was added, the mixture stirred for a few minutes with a ball-tipped glass rod and then extracted by suction. After the suction had been stopped, 50 cc. more of the KCl solution was added and the treatment was repeated until 10 extractions had been made. Then the ammonia determination was made as usual on the combined filtrates. The results from two similar experiments with peat loam soils are brought together in table 13. The filtered extracts of both these soils being quite yellow, no examination with Nessler's reagent was made.

Table 13 shows the sufficiency of 10 extractions for the quantitative recovery of the ammonia added from both of the peat soils. The method being satisfactory, no experiments were made to find out if the same results might be had with fewer extractions.

For all the blank samples the new method has given very low ammonia figures. It is to be noticed, however, that hardly one of the examinations was made directly on fresh soil but at first on soil which for a shorter or longer time had been stored in the laboratory. As some of the soils had been dried to such an extent that they could be easily sifted, all the conditions for a rapid nitrification were present, and of course the ammonia nitrogen was used up in this process. Since the ammonia added was recovered from the soils

TABLE 15

Results of single-extracting experiments with 0.5N KCl

NUMBER AND DEPTH OF THE SOIL SAMPLE	SOIL	AMMONIA NITROGEN			
		Added per 100 gm. soil	Found	Lost	
		mgm.	*mgm.*	*mgm.*	*per cent*
Soil I; 0–20 cm.....	Silt loam	0.00	0.00	....	.....
		50.26	46.60	3.66	7.28
Soil II; 0–20 cm.....	Heavy clay	0.00	0.00	....	.....
		50.26	44.29	5.97	11.89
Soil V; 0–20 cm.	Sand	0.00	0.00	....	.....
		50.26	50.05	0.21	0.43
Soil VI; 0–20 cm.....	Loam	0.00	0.00	....	.....
		50.26	48.09	2.17	4.32

examined, with the exceptions noted, the low ammonia figures of the blank soils are good proof that the organic nitrogen soil compounds are not attacked by this method.

Lemmermann and Fresenius (17), as well as Ruprecht and Morse (22), have found that lime (in the form of $CaCO_3$) is one of the factors contributing to the ammonia-adsorbing power of soil. As all the soils here examined were neutral or acid this point remained to be examined. For that reason the following experiment, reported in table 14, was made with soil V. Two samples, of 25 gm each, were mixed with 2 gm. of finely ground $CaCO_3$, after which a solution of $(NH_4)_2SO_4$ was added. After 1 hour one sample was extracted successively with 0.5 *N* KCl. To the other sample 50 cc. of ammonia-free HCl was added in an amount equivalent to the lime previously used. Since the solution had been decanted to the filter, the extractions were continued successively with 0.5 *N* KCl. In both cases the tenth extract was free from ammonia.

Though the lime was supplied in an amount much greater than is ever used in practice, its effect was quite unimportant. However, as better results were obtained in the case where the lime was transformed into chloride, it will be good to neutralize the alkaline soils with hydrochloric acid before starting the extractions.

It was discovered only after these and later experiments had been made that Tarassoff (24) had already determined soil ammonia by extracting it with a KCl solution. His method was as follows: 500 gm. of soil was shaken in a 1-liter cylinder with 800 cc. of 5 per cent solution of KCl. Thereupon the whole content of the cylinder was brought cautiously to a filter and the soil carefully washed with the solution of KCl. The consecutive portions of the filtrate were analyzed separately by distilling with MgO. With black soils rich in humus this method gave *more*, and with clay soils *less*, ammonia nitrogen than did Schlösing's method. Tarassoff, however, made no control experiments with the addition of ammonia nitrogen and it seems to be very unlikely that the method used in such a case would have been satisfactory,

TABLE 16

Results of experiments with the extracting ratio 1:4

AMMONIA NITROGEN			
Added per 25 gm. soil	Found	Lost	
mgm.	*mgm.*	*mgm.*	*per cent*
0.00	0.07	....	....
2.48	2.52	0.03	1.21
12.39	12.32	0.14	1.13

at least with a reasonable quantity of solution. König (16) seems to be of the opinion that in the treating of soil with a KCl solution all the ammonium compounds are brought into solution in one extraction by means of an interchange of ions. That this view cannot be correct and that, on the contrary, a definite equilibrium will exist between the soil and the extracting agents, appears from the result, reported in table 9, of a single extracting experiment on soil II with 1 *N* KCl. In order to illustrate this question the single extracting experiments with 0.5 *N* KCl (table 15) were made. In this the extracting ratio 1:2, i.e. 1 part of soil and 2 parts of solution, and the same procedure, were used as in the earlier single extracting experiments.

Thus it has happened that only with the sandy soil was all the ammonia liberated quantitatively; while with the other soils a part of the added ammonia is fixed in some manner.

For peat soils there is no reason to change the present successive procedure with the extracting ratio 1:2, but for mineral soils this manner takes considerable time, as sometimes up to 15 extractions are required before all the ammonia is liberated. By increasing the extracting ratio, for example to 1:4, a quicker extraction is to be expected partly because a little more of the am-

monia is extracted in each extraction, as experiments with single extractions have shown, and partly because the absolute amount of ammonia already liberated, which remains in the beaker after each decantation to the filter, is reduced. Since soil II retained the ammonia more obstinately than any other surface soil (table 12), the following experiment was made with it, the data of which are given in table 16. Twenty-five gm. of the soil was placed in a 250-cc. beaker and 12.5 cc. of a solution of $(NH_4)_2SO_4$ or 12.5 cc. of water added. After 1 hour the successive extractions were made in the same manner as before, but with 100-cc. portions of 0.5 *N* KCl. After 7 extractions, which required 5 hours, the liberation of ammonia was completed. Thus by enlargement of the extracting ratio from 1:2 to 1:4, the number of extractions could be reduced one-half.

FURTHER EXPERIMENTS WITH THE HEAVY CLAY SOIL (NO. II)

As pointed out before, the ammonia added could not be recovered from the lower layers of the heavy clay soil (table 12). For the layer 15 to 25 cm. the loss was relatively small but for the lowest layer (25 to 35 cm.) it was very considerable Experiments both with 20 and 30 successive extractions (in the extracting ratio 1:2) could not alter this result. The three samples from the layers 5 to 15, 15 to 25 and 25 to 35 cm., hereafter referred to as A, B, and C, respectively, had been cut out from one and the same block of soil, taken from a part of the field which had not been tilled during the last 9 months. These samples showed the pH values 6.2, 6.2 and 7.0 respectively. A chemical analysis gave the values indicated in table 17.

The organic matter was determined as loss after ignition minus H_2O. The K_2O, P_2O_5, CaO, and Al_2O_3 plus Fe_2O_3 were determined after digestion for 1 hour with 20 per cent HCl. Assimilable lime was obtained after treatment with a 10 per cent solution of NH_4Cl.

The most remarkable differences between the three samples from the chemical point of view are that the percentage of organic matter decreases with the depth of soil, whereas the percentage of Al_2O_3 plus Fe_2O_3 varies somewhat in the reverse order.

The experiments with soil C presented in table 18 were made by means of the successive extracting procedure in the extracting ratio 1:2. In all cases 12.5 cc. of $(NH_4)_2SO_4$ solution or an equal volume of water was added to 25 gm. of soil and then stirred from time to time for 1 hour. In one experiment (no. 1 and 2) the first extraction was made with 50 cc. of ammonia-free 0.5 *N* HCl. This was intended partly to reduce the pH value of the soil, as this soil had a higher pH value than the extractable soil A, and partly to diminish the percentage of Al_2O_3 plus Fe_2O_3. In the next experiment (no. 3 and 4) 5 gm. of soil III, earlier found to be free from ammonia, was added immediately before extracting in order to increase the percentage of organic matter. In the third experiment (no. 5 and 6), 5 gm. of soil III and 10 gm. of sand were added at the same time. In agricultural practice sand and mould are

added to clay soils in order to diminish the great cohesion in the clay and to counteract its tendency to pack or puddle. In the fourth experiment (no. 7 and 8) the extractions were made at a temperature of 3 to 5°C. on account of McBeth's results (19) from investigations concerning the influence of temperature on ammonia adsorption. Having stood for 1 hour at room temperature with 12.5 cc. of $(NH_4)_2SO_4$ or 12.5 cc. of water, these samples were placed

TABLE 17

Chemical analyses of heavy clay soil II

SOIL	PER CENT OF AIR-DRIED SAMPLE		PER CENT OF DRY MATTER						
	Particles > 2 mm.	H_2O	Organic matter	Total nitrogen	K_2O	P_2O_5	CaO	$Al_2O_3 + Fe_2O_3$	Assimilable CaO
A	0.70	12.90	8.01	0.29	0.74	0.31	1.06	9.65	0.50
B	0.35	13.21	7.52	0.28	0.78	0.27	1.08	9.90	0.50
C	0.23	12.17	5.00	0.17	0.70	0.21	1.12	11.20	0.55

TABLE 18

Results of extracting experiments with heavy clay soil II from depth of 25 to 35 cm.

NUMBER	AMMONIA NITROGEN				NOTES
	Added per 25 gm. soil	Found	Lost		
	mgm.	*mgm.*	*mgm.*	*per cent*	
1	0.00	0.28	....	.....	Extraction 1 made with 0.5 *N* HCl
2	12.57	10.43	2.42	19.26	
3	0.00	0.11	....	.....	Addition of 5 gm. of peat soil
4	12.41	9.73	2.79	22.48	
5	0.00	0.11	....	.....	Addition of 5 gm. of peat soil plus 10 gm. of sand
6	12.41	9.73	2.79	22.48	
7	0.00	0.21	....	.....	Extractions made at 3–5°C.
8	12.60	10.36	2.45	19.45	
9	0.00	0.11	....	.....	Extractions made with 3*N* KCl
10	12.41	10.08	2.44	19.67	

in ice water and then the extractions were made with KCl solution, previously cooled down to about 3°C. An experiment (no. 9 and 10), also was conducted in which the extractions were made with 3 *N* KCl in order to show that an increase of the concentration of the extracting agent is without any effect. In all these experiments the fifteenth filtrate was free from ammonia.

Thus this soil retains a rather constant amount of the ammonia added irrespective of the method of treatment. Nor could this part be liberated

by increasing the temperature as found by a further experiment on the samples 7 and 8. When the related 15 extractions had been made these samples were placed at the steam bath and stirred with 50 cc. of KCl solution, previously heated to 80°C. The samples then were allowed to settle on the bath, whereupon the extracts were decanted to the filter, 5 similar extractions being made. In no case was ammonia liberated by this procedure.

Finally, mechanical analyses of the soils A, B and C were made, giving the percentages shown in table 19. At first the gravel was sifted off and therefore the results refer to particles less than 2 mm. in diameter.

The table shows that the most remarkable difference between the samples exists in the percentage of clay, soil C holding about 13 per cent more of clay than the others. Naturally this higher percentage of clay in itself cannot be sufficient to account for the ammonia retention. The mechanical analysis gives no information, beyond the upper limit, of the size of the clay particles, but because of sedimentation the percentage of the smallest clay

TABLE 19

Mechanical analyses of heavy clay soil II

SOIL	SIZE OF PARTICLES						
	2–0. 6 mm.	0. 6–0.2 mm.	0, 2–0.06 mm.	0, 06–0.02 mm.	0, 02–0.006 mm.	0.006–0, 002 mm.	<0. 002 mm (clay)
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
A	1.79	6.17	13.17	11.18	10.05	11.72	45.92
B	1.85	7.00	13.12	10.60	10.00	12.35	45.08
C	2.01	5.21	10.07	9.93	9.30	12.14	51.34

particles may increase with the depth of the soil layer. The fixation of a part of the added ammonia by soil C therefore may probably be attributed to the surface effect of the very finest clay particles.

On the basis of the results the following method for determination of ammonia in surface soils is presented:

Mineral soils. In a 200 to 250 cc. beaker, 25 gm. of soil is stirred for a few minutes with 100 cc. of 0.5 *N* KCl solution free from ammonia. After settling, the solution is decanted to a filter of 100 cc. capacity. Then 100 cc. of the KCl solution is added to the beaker again and the treatment is repeated until the filtrate gives no coloration with Nessler's reagent. Even for soils which in consequence of colored filtrates do not permit examination with this reagent, not more than seven successive extractions are required. Alkaline soils should first be neutralized with ammonia-free hydrochloric acid. Then the combined filtrates are distilled with MgO, the ammonia being caught in 0.1 *N* H_2SO_4. When distillation is finished the carbon dioxide is removed from the distillate by boiling, and after cooling the distillate is titrated with 0.1 *N* NaOH, methyl red being used as the indicator. A blank determination should be made on the reagents.

Peat soils. Twenty-five grams of soil is placed on a hardened filter in a Büchner funnel fixed to a suction flask, and 50 cc. of 0.5 *N* KCl solution is added. The soil is then stirred by means of a ball-tipped glass rod, after which the solution is sucked off. Then the suction is stopped and 50 cc. of the KCl solution is added again to the soil, whereupon the treatment is repeated until all the ammonia is extracted. Not more than 10 extractions are required at the most. The ammonia determination is performed in the same manner as for the mineral soils.

By extracting with 0.5 *N* KCl solution containing 1 to 5 gm. of $HgCl_2$ per litre, the work can be interrupted without any risk of ammonification and finished another day. In this case the mercury must be precipitated as HgS before the distillation. A disadvantage following the use of KCl solution containing $HgCl_2$ is that this solution, even if free from ammonia, gives a brown precipitation with Nessler's reagent.

Of course there is no objection to working with a larger quantity of soil, in order to obtain better mean values. In such a case the KCl portions must be increased in corresponding degree.

SUMMARY

1. A reëxamination of the methods of Boussingault, Baragiola and Schuppli, Potter and Snyder, Matthews and that of Gibbs, Neidig and Batchelor for the determination of ammonia in soil showed that none of them was able to recover added ammonia quantitatively. This was true for both surface soils and subsoils.

2. Steinkopf's steam distillation was not suitable for the purpose in question.

3. Experiments with different extracting agents showed that as a rule it is not possible to bring all the added ammonia into solution in one extraction. Therefore, the methods of Schlösing and Valmari cannot be of general application.

4. As to the liberation of added ammonia, a solution of potassium chloride was found to be the most effective of the extracting agents examined.

5. Added ammonia was recovered quantitatively from *surface soils* by means of a successive extracting procedure.

By this method, in case of a mineral soil, 25 gm. of soil is extracted successively with, at the most, seven 100-cc. portions of approximately 4 per cent potassium chloride solution. With peat soils, 25 gm. of soil is extracted in a similar way with at most ten 50-cc. portions of the same solution.

The very low ammonia values found by this method for untilled arable soils are strong evidence that organic nitrogen compounds of soil are not split during the analysis.

6. The successive extracting procedure was not satisfactory in case of a heavy clay subsoil taken from the depth of 25 to 35 cm. This may be attributed to the surface effect of the very finest clay particles.

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THE INFLUENCE OF PHOSPHATE, BIPHOSPHATE, CARBONATE, SILICATE AND SULFATE OF CALCIUM, SODIUM AND POTASSIUM ON PLANT GROWTH IN ACID MINERAL SOILS

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Received for publication March 3, 1924

INTRODUCTION

The study of the nature and the improvement of acid mineral soil is very important to the agriculture in our country where acid mineral soil is widely distributed. (13, 27, 49).

Though there are many opinions about the cause of the acidity of soil, (15, 18, 19, 20, 21, 25, 26, 30, 39, 41, 42, 53, 55, 58, 59) it seems to be recognized that aluminium is present in greater amount in acid soil than in non-acid soil and is concerned directly or indirectly with its acidity (1, 13, 22, 32, 34, 35, 37, 38, 42, 43, 44, 46, 52). The toxic action of aluminium upon plant growth has been well proved by various authors (9, 11, 17, 24, 28, 31, 33, 56, 60). Abbott, Conner and Smalley (1) studying the cause of unproductive acid soil of Indiana, found that a relatively large amount of aluminium was dissolved out in the soil extract and that the toxicity of the extract was equal to the toxicity of nitric acid and aluminium nitrate of the same normality. Ruprecht and Morse (44) found that aluminium sulfate formed by the continual application of ammonium sulfate is the cause of unproductivity of soil. Hartwell and Pember (23) also found that aluminium is the element responsible for the depression of the growth of barley. Mirasol (32) also confirmed, this effect on the growth of sweet clover. Blair and Prince (4) recently found that aluminium present in great amount in the soil solution extracted by distilled water, is the cause of toxicity of soil.

Aluminium can not be neglected as one of greatest factors causing unproductivity of acid soil, though there may be some other injurious factors such as lack of plant nutrients. The elimination of active aluminium through changing it into an insoluble form by the addition of lime or other salts, therefore, should bring some favorable effect upon the plant growth. Studying the effect of silicates upon the growth of plants in acid soil, Cowles (12) and Scheidt (45) reported that dicalcium silicate had a relatively greater value than either ground limestone or calcium hydrate as a fertilizer material. Hartwell and Pember (23), and Schollenberger (47) also reported that plants made a favorable growth by the application of dicalcium silicate to acid soil. Conner (8)

reported that dicalcium silicate gave better results in field and pot experiments than those obtained by the use of lime. The superior effect of silicate was attributed to the elimination of aluminium as aluminium silicate from the soil solution. The effect of the addition of calcium carbonate to acid soil also is well known. As to the cause of its favorable effect, Ruprecht and Morse (44) suggested that aluminium in soil is precipitated as hydroxide upon the addition of calcium carbonate, and as such has no effect on plant growth. Mirasol (32) reported also that the good effect of carbonate for the correction of unproductive acid soil is due to the elimination of active aluminium because when calcium carbonate is added to acid soil aluminium is transformed into some very stable compound such as calcium aluminate. The favorable effect of phosphate upon the growth of plants in the acid soil also is a well known fact, since the addition of phosphates is believed to cause the formation of the very insoluble aluminium phosphate, otherwise it acts upon the plant growth harmfully. After the investigation of the effect of the addition of biphosphate, Hartwell and Pember (22) found that the amount of active aluminium was decreased and barley made remarkable growth. Mirasol (32) studied the same subject and reported that sweet clover also made marked growth by the addition of biphosphate to the acid soil.

Thus, the elimination of soluble aluminium existing in acid soil is a very important phase of the problem of improving unproductive acid soil. Thus the addition of some chemicals which make aluminium insoluble is expected to be favorable to plant growth. The investigations hitherto conducted, however, are not, satisfactory regarding this phase of the problem. The investigators have not paid any attention to the power of the chemicals used to make aluminium insoluble. Then, we have undertaken the experiment for the purpose of throwing more light upon the general problem of aluminium in acid soils, and also to explain why phosphate fertilizer has a good effect on such soil.

EXPERIMENT I

The depression of the toxic action of aluminium compounds would be expected to correspond with the power of the various chemicals which convert the soluble into the insoluble compounds, and the favorable action of the various chemicals upon the plant growth should be due to this power. Also, it is important to know how much soluble aluminium is converted into insoluble by the addition of the chemicals andt heir relation to the plant growth. In order to throw some light upon these questions, an experiment was conducted on the use of the phosphate, biphosphate, carbonate and silicate of sodium.

At first the amount of insoluble aluminium produced by mixing a solution of equal volume of 0.2N or 0.1N aluminium chloride and 0.2 N or 0.1 N sodium silicate, sodium carbonate, sodium phosphate and sodium biphosphate was determined as a measure of the power of these chemicals to convert the soluble into the insoluble compound. The results are given in table 1.

The composition of the aluminium silicate produced from the mixture of aluminium chloride and sodium silicate was not definite. While a large amount of silica was precipitated, the amount of precipitated aluminium was very small. This may be due to either the fact that the form of aluminium silicate is very complex, or that silica is liberated from sodium silicate by the action of hydrochloric acid formed by the hydration of aluminium chloride and precipitated with aluminium silicate. No insoluble aluminium was obtained from the mixed solution of sodium biphosphate and aluminium chloride. It was observed that 30 per cent of the original aluminium and phosphoric acid was precipitated from the mixed solution of sodium phosphate and aluminium chloride. This small amount of the precipitate produced may be due to the acid reaction of the mixture. The amount of aluminium pre-

TABLE 1

Amount of aluminium precipitated from mixed solution of 100 cc. of aluminium chloride and 100 cc. of sodium silicate, sodium carbonate, sodium phosphate or sodium biphosphate

CONSTITUENTS MEASURED	NAME OF MIXED SALTS			
	Sodium silicate + aluminium chloride	Sodium carbonate + aluminium chloride	Sodium phosphate + aluminium chloride	Sodium biphosphate + aluminium chloride
	A—0.2 *N* Salts			
	gm.	*gm.*	*gm.*	*gm.*
P_2O_5	—	—	0.1447	—
SiO_2	0.1810	—	—	—
Al_2O_3	0.0220	0.3400	0.0973	—
	B—0.1 *N* Salts			
	gm.	*gm.*	*gm.*	*gm.*
P_2O_5	—	—	0.0871	—
SiO_2	0.1184	—	—	—
Al_2O_3	0.0232	0.1634	0.0566	—

cipitated in this case, however, was larger than that precipitated from the mixed solution of aluminium chloride and sodium silicate. In the case of mixing aluminium chloride and sodium carbonate, the entire amount of aluminium was precipitated, the reaction of the mixture being alkaline.

In order to confirm these phenomena as occurring in the soil, in the next experiment these solutions were added to the acid soil, and then a soil solution was prepared with water five times the weight of the soil. The amounts of alumina, silica and phosphoric acid in the solution were measured, with following results in table 2.

When sodium carbonate solution was added to the soil which had been treated with aluminium chloride solution, aluminium was scarcely found in the soil solution. The alkalinity of sodium carbonate was higher than of phosphate and silicate of sodium, and therefore a large amount of aluminium was

precipitated and retained in the soil as compared with the latter two salts. When 0.2*N* sodium phosphate was used, one-thirteenth of the original aluminium which had been added to the soil was dissolved out while no phosphoric acid was found in the solution extracted from the soil. When 0.1 *N* sodium phosphate was used, neither aluminium nor phosphoric acid was detected. When 0.2*N* or 0.1*N* sodium biphosphate was added, one-third of the original amount of aluminium which had been added to the soil was found again in the solution, a trace of phosphoric acid. Though biphosphate could not produce

TABLE 2

Amount of aluminium in the solution extracted from 200 gm. of soil with five times its weight of water

(1) 100 cc. aluminium chloride and 100 cc. sodium silicate, sodium carbonate, sodium phosphate or sodium biphosphate added.

CONSTITUENTS MEASURED	NAME OF MIXED SALTS			
	Sodium Silicate + aluminium chloride	Sodium carbonate + aluminium chloride	Sodium phosphate + aluminium chloride	Sodium biphosphate + aluminium chloride
	A—0.2 *N* Salts			
	gm.	*gm.*	*gm.*	*gm.*
P_2O_5	—	—	—	Trace
SiO_2	0.0340	Undetermined	Undetermined	Undetermined
Al_2O_3	0.1540	—	0.0200	0.1046
	B—0.1 *N* Salts			
	gm.	*gm.*	*gm.*	*gm.*
P_2O_5	—	—	—	Trace
SiO_2	0.0230	Undetermined	Undetermined	Undetermined
Al_2O_3	0.0440	—	—	0.0534

(2) 100 cc. of aluminium chloride solution only added

NORMALITY	CONSTITUENTS MEASURED	AMOUNT OF ALUMINA PRESENT IN ORIGINAL SOLUTION	AMOUNT OF ALUMINA PRESENT IN EXTRACTED SOLUTION
		gm.	*gm.*
0.2 *N*	Al_2O_3	0.3680	0.2640
0.1 *N*	Al_2O_3	0.1840	0.0880

any precipitate of aluminium phosphate from aluminium chloride and sodium biphosphate in the solution, a relatively great amount of aluminium was precipitated in the case of the soil. It was known further from the results that almost the total amount of phosphoric acid was retained in the soil without relation to the amount of aluminium retained, when sodium phosphate or sodium biphosphate was added with aluminium chloride. When 0.2 *N* sodium silicate was used, one-ninth and two-thirds, respectively, of the original amount of silica and aluminium which had been added to the soil were found in the soil solution. And when 0.1*N* solution also was used, one-seventh and one-half

of the original amount of silica and aluminium, respectively, were detected in the soil solution. It was observed, therefore, in this case, that a large amount of aluminium which had been added was dissolved out again in the soil solution without being retained with silica in the soil. Although, the reaction of sodium silicate in the solution is more alkaline than that of sodium phosphate and biphosphate, the former could not precipitate the aluminium as much as the latter two salts, except when 0.1 *N* of sodium biphosphate was used.

When aluminium chloride solution only was added to the soil, one-fourth to one-half of original amount of aluminium was retained by the soil; but this was smaller than that held after the addition of sodium carbonate, sodium phosphate, sodium biphosphate or sodium silicate. From this it is clear that some soluble aluminium in the soil is transformed into insoluble and retained in it by the addition of carbonate, phosphate, biphosphate and silicate of sodium. The order of the salts in precipitating aluminium in the solution is—carbonate, phosphate and silicate, while the order in bringing aluminium into insoluble form in the soil is—carbonate, phosphate, biphosphate and silicate.

EXPERIMENT II

It is reported that the addition of the carbonate, phosphate, biphosphate and silicate of calcium and sodium in pot and field experiments with acid soil, stimulated plant growth. The favorable effect, however, is not yet clearly explained. We may expect from the results of our experiment that the change of solubility of the aluminium compounds brought about by the addition of the salts is one of the main causes of this good effect, the measure of which is the power of the salts to transform the soluble into the insoluble form, though some difference caused by the other factors may exist between the calcium and the sodium compounds.

In order to compare the action of calcium with sodium in practice, we conducted a pot experiment in which acid soil collected from province Kutchan was used. The carbonate, phosphate, biphosphate and silicate of calcium, sodium and potassium were selected for the test. In addition to these the sulfate was tested, its application having been reported to make the soil unfavorable to the plant growth by increasing the amount of soluble aluminium.

Daikuhara (13), and Osugi (35) (36) proved that the soil acidity measured by the potassium chloride method corresponds generally with the quantity of aluminium precipitated by titration with alkali. While this amount of aluminium may not indicate the amount of active aluminium which is toxic to the growth of plants in the soil, it may be expected that the greater the amount of the former, the greater also is the amount of the latter. Then, if this aluminium might be changed into an insoluble form, the amount of toxic aluminium will be decreased. According to this supposition, the equivalent quantity of phosphate, biphosphate, carbonate, silicate and sulfate of calcium, potassium and sodium corresponding to the acidity of the acid soil was calculated as shown in table 3, and was added to the pots each holding 1670 gm. of

the soil, for the purpose of changing the aluminium into insoluble or more soluble forms. The acidity of the soil was measured by the potassium chloride method and it was found to be neutralized by 75 cc. of 0.1*N* NaOH per 100 gm. of the soil.

After the addition of various salts to the soil, 28 seeds of barley were sowed on May 1. On May 18 the growing plants in each pot were thinned to 4 plants of the same growth. The height of the plants was measured on June 15 and 20, and when the barley was harvested on July 28, the length and weight of the plant, the length of the ear and the weight of the seed were measured. Also, the plants were photographed on June 15, and July 28, as shown in plates

TABLE 3

The weight of phosphate, biphosphate, carbonate, silicate and sulfate of calcium, potassium and sodium equivalent to the acidity of 1670 gm. of Kutchan acid mineral soil

POT NUMBER	SALTS USED	WEIGHT OF SALTS
		gm.
1	$CaCO_3$	4.7585
2	$CaHPO_4$	4.3186
3	$CaSiO_3$	5.5198
4	$CaSO_4$	8.1893
5	$CaH_4P_2O_8$	3.7147
6	K_2CO_3	6.5810
7	K_2HPO_4	4.2882
8	K_2SiO_3	7.3614
9	K_2SO_4	8.2998
10	KH_2PO_4	4.3113
11	Na_2CO_3	5.0487
12	$NaHPO_4$	3.7775
13	Na_2SiO_3	7.1736
14	Na_2SO_4	6.7633
15	NaH_2PO_4	3.8093

1 to 3. After the harvest, the acidity of the soil in which the barley had been planted was measured by potassium chloride method, as well as the quantity of aluminium precipitated by titration with alkali. In this case iron was mixed in the aluminium precipitate, but since its amount was quite small, it was not measured, and the total sum of alumina and iron oxide was shown as alumina. The pH value of the soil solution also was measured by Clarke and Lubs method (6). The soil solution used for the determination of H-ion concentration was made by centrifuging the extract from 100 gm. soil to which 200 cc. of water was added. The results are shown in table 4.

The carbonate reduced the acidity of the soil from the original figure of 58.8 to 16.2–26.4 phosphate to 16.8–26.4; biphosphate to 31.6 and silicate 39.6–41.4, but the sulfate had less effect, reducing the acidity only to 46.7–

60.0. As in the case of American soils mentioned by Gillespie (18), and Sharp and Hoagland (48), the pH value of the Kutchan acid soil was very low, but the pH value of the soil solution treated with the various salts appeared to be higher than that of the untreated. But its change did not correspond with the soil acidity measured by the potassium chloride method. In the case of phosphate the pH value was 6.0 to 5.9; biphosphate, 6.0 to 5.7; carbonate, 5.9 to 5.6; silicate, 5.9 to 4.9; and sulfate, 5.0 to 4.8. The order of elevation of the pH value as influenced by the addition of the salts is: phosphate, carbonate,

TABLE 4

Growth of barley in Kutchan acid mineral soil treated with carbonate, phosphate, biphosphate, silicate and sulfate of calcium, potassium or sodium.

NUMBER OF POT	LENGTH OF STEM			TOTAL WEIGHT	LENGTH OF EAR	WEIGHT OF SEED	NUMBER OF CULMS PER POT
	June 15	June 20	July 28	July 28	July 28	July 28	July 28
	cm.	*cm.*	*cm.*	*gm.*	*cm.*	*gm.*	
0*	13.3	15.8	30.6	0.50	—	—	4
1	19.7	26.1	52.1	4.00	3.3	1.75	4
2	34.2	44.5	90.0	14.00	7.6	2.25	11
3	12.1	13.9	31.2	1.50	—	—	4
4	15.2	20.4	21.5	1.0	—	—	4
5	34.8	42.1	91.8	13.5	8.7	2.25	11
6	19.4	22.1	44.0	2.25	2.7	1.25	4
7	36.7	38.2	59.8	12.00	6.0	3.25	10
8	32.1	21.8	34.5	2.25	2.3	1.75	4
9	9.1	9.3	9.4	0.25	—	—	4
10	37.6	39.1	80.1	15.00	8.8	3.35	14
11	19.0	19.7	45.1	2.50	3.6	1.25	4
12	38.4	44.2	79.8	16.00	7.6	2.75	9
13	17.2	21.8	41.8	3.00	3.0	0.75	4
14	11.2	12.6	14.2	0.75	—	—	4
15	38.7	44.3	81.4	15.25	9.9	3.75	9

*Control.

biphosphate, silicate and sulfate, from the standpoint of cation; and sodium, potassium and calcium from the standpoint of anion.

The amount of aluminium precipitated by the titration with alkali nearly coincides with the acidity of the soil except in the case of the addition of sulfate.

The phosphate additions had a good influence upon the growth of the plant. In spite of its acid nature, biphosphate also caused a marked plant growth. When carbonate or silicate was added, the growth of barley was better than the untreated, but not as good as with phosphate and biphosphate.

The sulfate-treated pots were rather worse than the untreated, since half or all of the barley in every pot died. The amount of the culm was greatest in the soil treated with phosphate or biphosphate, followed by the carbonate or silicate-treated pots. In the case of carbonate, silicate and sulfate the growth of barley was increased with the decrease in the soil acidity. The acidity of the soil treated with carbonate nearly coincided with that of the phosphate-treated soil while it was lower than in the case of biphosphate. But the plant growth in the soil treated with the latter two salts was remarkably better than in the soil to which the first had been applied.

TABLE 5

The pH value, the acidity of the soil and the amount of aluminium precipitated by titration with alkali

POT NUMBER	pH VALUE, CLARK AND LUBS METHOD	ACIDITY, POTASSIUM CHLORIDE METHOD	ALUMINIUM PRECIPITATED BY TITRATION WITH ALKALI
			gm.
0	4.2	58.8	0.0362
1	5.6	16.2	0.0100
2	5.9	16.8	0.0117
3	4.9	41.4	0.0275
4	4.8	60.9	0.0467
5	5.3	31.6	0.0217
6	5.8	26.4	0.0162
7	5.9	26.4	0.0171
8	5.3	39.6	0.0249
9	5.1	50.6	0.0403
10	5.8	31.6	0.0220
11	5.9	21.3	0.0140
12	6.0	23.0	0.0149
13	5.5	41.4	0.0265
14	5.0	46.7	0.0373
15	6.0	31.6	0.0220

EXPERIMENT III

From the above it is clear that the addition of phospate or biphosphate to the acid soil was the most favorable for plant growth. For the purpose of making clear the influence of the phosphate upon the barley in acid soil, further study was conducted. In this case Kutchan and Tayoro acid mineral soils were used, to which was added 0.1 gm. of nitrogen per pot as the source of nitrogenous plant-food in the form of ammonium sulfate. In order to avoid the influence of acid liberated from the ammonium sulfate after the ammonia is absorbed by the plant or the soil, calcium carbonate equivalent to the ammonium sulfate also was added. To one series of the pots, besides the above

two salts, potassium phosphate in an amount corresponding to 0.1 gm. of phosphoric acid was added per pot as the source of phosphatic plant-food, and in the other series it was omitted. Then, to the pots of these two series potassium phosphate, potassium silicate, sodium silicate or calcium carbonate in the amount equivalent to the soil acidity was added, calculated as shown in table 6.

TABLE 6

The weight of the salts added to the soil

POT NUMBER	AMOUNT OF SALTS ADDED AS NUTRIENT PER POT		AMOUNT OF $CaCO_3$ EQUIVALENT TO AMMONIUM-SULFATE ADDED PER POT	SALTS ADDED PER POT EQUIVALENT TO ACIDITY	
	$(NH_4)_2SO_4$	K_2HSO_4		Name	Weight
Kutchan acid mineral soil; 1670 gm. per pot; acidity—75					
	gm.	*gm.*	*gm.*		*gm.*
B1	0.95	—	0.7143	—	—
B2	0.95	—	0.7143	$CaCO_3$	4.7595
B3	0.95	—	0.7143	K_2HPO_4	4.2882
B4	0.95	—	0.7143	K_2SiO_3	7.3614
B5	0.95	—	0.7143	Na_2SiO_3	6.7633
C1	0.95	0.49	0.7143	—	—
C2	0.95	0.49	0.7143	$CaCO_3$	4.7595
C3	0.95	0.49	0.7143	K_2HPO_4	4.2882
C4	0.95	0.49	0.7143	K_2SiO_3	7.3614
C5	0.95	0.49	0.7143	Na_2SiO_3	6.7633
Tayoro acid mineral soil; 1025 gm. per pot; acidity—103.5					
A1	0.95	—	0.7143	—	—
A2	0.95	—	0.7143	$CaCO_3$	5.2256
A3	0.95	—	0.7143	K_2HPO_4	5.7810
A4	0.95	—	0.7143	K_2SiO_3	8.1313
A5	0.95	—	0.7143	Na_2SiO_3	6.9357
B1	0.95	0.49	0.7143	—	—
B2	0.95	0.49	0.7143	$CaCO_3$	5.2256
B3	0.95	0.49	0.7143	K_2HPO_4	5.7810
B4	0.95	0.49	0.7143	K_2SiO_3	8.1313
B5	0.95	0.49	0.7143	Na_2SiO_3	6.9357

After the germination of 28 seeds, 4 plants of barley were retained in each pot of the Kutchan acid soil. In the case of Tayoro acid soil the plants were thinned to 3. The experimental treatment and observation also were the same as in the former experiment.

The results obtained are presented in table 7 and 8, and the relative growths of the plants is shown in plates 4 to 7.

In these experiments, the acidity of the series which received phosphoric acid as plant-food was lower than that of the other series. The acidity of the

soil was decreased in each series when phosphate or carbonate was added, while the rate of decrease caused by the salts was almost similar in the case of Kutchan acid soil but in Tayoro acid soil, carbonate reduced the acidity much more than phosphate. Silicate also reduced the acidity of the two kinds of

TABLE 7

Growth of barley in Kutchan and Tayoro acid mineral soil treated with sulfate, phosphate, silicate, or carbonate

POT NUMBER	LENGTH OF STEM			TOTAL WEIGHT	LENGTH OF EAR	WEIGHT OF SEED	NUMBER OF CULMS PER POT
	June 15	June 20	July 28	July 28	July 28	July 28	July 28
Kutchan acid mineral soil							
	cm.	*cm.*	*cm.*	*gm.*	*cm.*	*gm.*	
0	13.3	15.8	30.6	0.50	—	—	4
B1	15.1	16.4	30.6	1.25	—	—	4
B2	17.2	17.3	34.4	2.5	2.1	1.25	4
B3	23.3	26.9	50.6	4.75	6.3	1.25	4
B4	18.3	19.1	34.5	1.5	—	—	4
B5	16.9	19.1	30.6	1.0	1.2	0.10	4
C1	17.2	18.8	34.0	1.0	—	—	4
C2	36.4	47.6	87.6	12.5	7.2	3.75	7
C3	47.5	49.1	80.6	24.5	8.7	6.0	12
C4	37.0	45.1	65.4	5.5	6.0	1.75	6
C5	30.0	36.4	53.6	6.5	6.0	0.25	5
Tayoro acid mineral soil							
0	16.1	17.0	27.9	0.5	—	—	3
A1	17.6	19.1	31.0	0.5	—	—	3
A2	30.6	32.4	69.9	9.5	7.5	2.25	3
A3	45.1	58.2	81.8	26.5	9.7	6.25	11
A4	29.9	35.4	53.7	5.5	4.8	1.00	3
A5	31.8	33.0	44.5	6.25	5.4	1.25	3
B1	16.7	19.9	20.3	1.25	3.6	0.25	3
B2	34.2	44.5	77.6	16.0	9.0	2.25	6
B3	45.8	51.6	86.8	35.0	10.5	7.75	15
B4	25.1	36.1	49.6	6.5	6.0	0.5	3
B5	29.7	43.3	51.5	7.5	7.5	0.75	3

acid soil, but its power was lower than that of phosphate. When ammonium sulfate was added, the acidity was decreased slightly, perhaps because of the excess of calcium carbonate present.

The pH value of Kutchan acid mineral soil was increased by the addition of phosphate. In Tayoro soil this difference of the pH value was a little greater

than that observed in Kutchan soil. The order of increase of the pH value due to the salts was: phosphate, carbonate and silicate.

The amount of aluminium precipitated by titration with alkali nearly coincided with the acidity of the soil.

The length and weight of stem, the length of ear and also the weight of seed increased in the soil treated with phosphate as a source of phosphatic plant-

TABLE 8

The pH value, the acidity of the soil and the amount of aluminium precipitated by titration with alkali

POT NUMBER	pH VALUE, CLARK AND LUBS METHOD	ACIDITY, POTASSIUM CHLORIDE METHOD	Al_2O_3 PRECIPITATED BY TITRATION WITH ALKALI
Kutchan acid mineral soil			
			gm.
0	4.2	58.8	0.0362
B1	4.8	47.8	0.0344
B2	5.2	20.1	0.0175
B3	5.3	20.7	0.0188
B4	5.0	21.9	0.0185
B5	5.3	37.4	0.0294
C1	5.0	43.2	0.0320
C2	6.0	16.2	0.0125
C3	6.2	16.2	0.0148
C4	5.7	20.1	0.0196
C5	6.0	34.2	0.0274
Tayoro acid mineral soil			
0	3.6	94.5	0.0571
A1	3.6	85.8	0.0607
A2	5.2	16.8	0.0168
A3	5.6	30.0	0.0239
A4	4.1	43.2	0.0331
A5	5.3	49.5	0.0268
B1	3.7	66.7	0.0498
B2	5.3	13.8	0.0147
B3	5.4	23.6	0.0191
B4	4.4	36.8	0.0279
B5	5.3	38.8	0.0306

food, as compared with the untreated while the plants made most marked growth in the soil treated with phosphate for the neutralization of the acidity. Carbonate also promoted the plant growth, followed in order by silicate. But no good result was obtained by the addition of ammonium sulfate and calcium carbonate only.

For the purpose of comparing the effect of various amounts of phosphate upon the growth of the plant, the results obtained with potassium phosphate in second and third experiments are brought together in table 9.

The growth of the plant greatly increased, while the amount of aluminium precipitated and the acidity of the soil were decreased, according to the amount of phosphate given, though the quantitative relation between the amounts was not strictly observed. It is evident at any rate that the plant made a decidedly marked growth from the application of a large amount of phosphate.

According to the results of the first experiment, a small amount of soluble aluminium was retained as insoluble in the soil by the addition of silicate as compared with phosphate, biphosphate and carbonate, although its reaction was more alkaline than that of phosphate and biphosphate. It may, then, be concluded that the poor plant growth in the case of silicate addition in

TABLE 9

The effect of various amounts of potassium phosphate upon plant growth and acidity, and the amount of aluminium precipitated

AMOUNT OF				LENGTH OF STEM	TOTAL WEIGHT OF PLANT	SOIL ACIDITY KCl METHOD	ALUMINIUM PRECIPITATED WITH ALKALI Al_2O_3
$(NH_4)_2SO_4$	$CaCO_3$	K_2HPO_4					
		As plant-food	As neutralizer				
gm.	*gm.*	*gm.*	*gm.*	*cm.*	*gm.*	*cc.*	*gm.*
Control	—	—	—	30.6	0.50	58.8	0.0362
0.96	0.7143	—	—	30.6	1.25	47.8	0.0344
0.96	0.7143	0.49	—	34.0	1.0	43.2	0.0320
0.96	0.7143	—	4.2882	50.6	4.75	20.7	0.0188
—	—	—	4.2882	59.8	6.0	26.4	0.0171
0.96	0.7143	0.49	4.2882	80.6	24.5	16.2	0.0145

experiments II and III, is attributable to the low power of silicate to eliminate soluble aluminium in the soil.

The favorable action of biphosphate, which is acid in nature, also may be explained by the fact that aluminium was retained in the soil as insoluble aluminium phosphate by the application of this salt, as shown in the first experiment, though it did not produce any precipitate of aluminium phosphate from the solution mixed with aluminium chloride and sodium biphosphate. Also the favorable influence of carbonate or phosphate may be explained by the fact that these salts retained in the form of inactive compounds the great amount of toxic aluminium present in the soil.

It is clear from the above that the elimination of active aluminium present in acid soil, is one at least of the favorable factors caused by these salts in plant growth. But, as shown in the pot experiment, the most favorable effect was not given by the chemicals which converted the soluble aluminium into the insoluble in greatest amount. The greatest amount of aluminium was

retained in the case of carbonate, but the plant did not make more marked growth from the application of this salt than with phosphate and biophosphate.

The favorable effect can not be explained, therefore, merely from the standpoint of the power of these salts to change soluble aluminium into insoluble. We must consider other factors.

The low pH value of the acid soil we tested was increased by the addition of the various salts, but the differences did not correspond with the change in soil acidity caused by the addition of the same salts. Though the plant generally made a more favorable growth according to the raising of the pH value of the soil solution, the plant growth and depression of the hydrogen-ion concentration of the soil solution did not strictly coincide. In some cases the plant made a good growth in soil of low pH value, while in others it could not live even under high pH value; hence pH value does not seem to be a great factor causing the unproductivity of acid soils.

The change of the acidity of the soil influenced by the addition of sulfate of calcium or potassium is reported by many authors, for example, Skinner and Beattie (51), Singh (50), Ames and Schollenberger (2), Conner (8), Erdman (16), Lipman (29), and Bear and Salter (3). Some of them observed that the acidity of the soil was increased by the addition of these salts, while others reported the opposite result. In our experiment, when sulfates were added to the acid soil the acidity was generally neither decreased nor increased. Perhaps, such differences found among the results of various authors may be attributed to the difference in the methods used for acidity determination. In some cases true acid was measured; in other cases the amount of aluminium which dissolved out from the soil by the salt added was observed as the acid. A difference also is caused by the amount of sulfate added to the soil, a small amount having no influence, while a large amount of sulfate greatly increases the acidity.

In our experiment the acidity of the soil was not decreased as much by the addition of silicate as we expected, while Conner (10) reported that the acidity was markedly decreased by the addition of dicalcium silicate. The effect of carbonates upon the soil acidity has been widely studied. In Japan Daikubara (14), Sibuya (49), Ishii (27) and others have observed the favorable influence of calcium carbonate for the neutralization of soil acidity. Osugi (35) also obtained good results from calcium and sodium carbonate in treating acid soil. We found the best effect came from the application of carbonate among the salts of the same cation. The decrease in soil acidity resulting from the addition of phosphate and biphosphate also has been thoroughly studied already by Veitch (58), Brook (5), Conner (8), Ames and Schöllenberger (2), Plumber (40) and Mirasol (32). In our experiments also it was found that the depression of soil acidity was brought about by the application of phosphate or biphosphate. The former salt decreased the acidity more than the latter, its degree of depression being almost similar to that of carbonate. The degree of depression caused by biphosphate was found to be greater than that by silicate.

Thus, the order of the depression of acidity brought about by the addition of the salts we tested was: carbonate, phosphate, biphosphate, silicate and sulfate. This order strictly coincides with that of the amount of aluminium retained in the soil by the salts observed in our first experiment. It seems that a certain correlation exists between the change of the acidity (measured by the potassium chloride method) brought about by the application of the salts, and the amount of aluminium converted into insoluble form by the use of these salts. In other words, the soil acidity is responsible to the amount of aluminium which is precipitated by the titration with alkali. Therefore, the salts which convert more aluminium into insoluble form also depress more largely the soil acidity.

As already stated, the plant growth in the soil treated with silicate was poorer than in that receiving phosphate, biphosphate, and carbonate, but better than in the untreated, while the plant in the soil treated with sulfate grew much more poorly than that in untreated. Except in the case of carbonate the growth of the plant depended upon the degree of depression of the soil acidity brought about by the addition of the salts. Though the addition of carbonate caused the greatest depression of acidity, the growth of the plant ranked next to that of phosphate or biphosphate. Then it seems that, though the change of acidity resulting from the use of silicate, carbonate, phosphate and biphosphate is a very important factor in the growth of plants in acid soils, in the case of phosphates it is not the sole factor favorably affecting plant growth.

If the plant growth corresponds with the degree of elimination of toxic aluminium only, caused by the addition of various salts, the soil treated with carbonate should prove most favorable to the plant. On the contrary, the plants have made marked growth in the soil treated with phosphate or biphosphate as compared with carbonate. Conner (10) explained that this inferiority of carbonate to phosphate is due to the solubility of aluminium hydroxide and phosphate in a solution of the same pH value, as hydroxide is dissolved more easily in a weak acid than phosphate. Thus the toxic action of aluminium, appears on the plant in the case of hydroxide more than with phosphate. But in our experiment the amount of aluminium dissolved out in the solution of potassium chloride by the determination of acidity from the soil treated with carbonate, was smaller than in the case of the soils treated with phosphate or biphosphate. This denotes that the more stable aluminium compound was formed in a greater amount in the former than in the latter soils, though the plant made poor growth in the former. We can not believe, therefore, that the difference of solubility of aluminium hydroxide and phosphate is a factor explaining the inferiority of carbonate, as stated by Conner. The good effect of the addition of phosphate or biphosphate might be explained by the special demand of this kind of soil for phosphoric acid as a plant-food. Then, the question arises—If the total amount of soluble phosphate or biphosphate added to the soil is converted into insoluble phosphate, how does it feed the plant?

In many reports it is mentioned that aluminium phosphate can feed plants, though the effect is not great, the salt being relatively insoluble. If this took place in our experiments, a great amount of aluminium phosphate must have been absorbed by the plant in the case of the soil treated with phosphate or biphosphate, for the plants made marked growth. If the opinion developed recently from the view of colloid chemistry is true, that the minute particles are passed through the membrane and absorbed in the plant body (7, 54), it may be that the minute particles of aluminium phosphate present in the soils behaved in this manner. If so, the plant would absorb at the same time with phosphoric acid a large amount of aluminium, which not only is not found in large amount in the plant body, but its existence in a large quantity is very toxic to plant growth. Such a thing, however, can not be considered. Then the utilization of phosphoric acid in such a case should be explained in some other way. Perhaps, a part of the phosphate added may remain in an absorbed form without resulting in the formation of aluminium phosphate, while the other form of phosphate available to plants may be produced by the mutual action of soil constituents with aluminium phosphate. Such phosphates would afford the phosphatic food of the plant in the soil. This phase, of the problem, however, needs further study.

SUMMARY

1. In this paper we have reported the results of our experiments on the behavior of phosphate, biphosphate, carbonate, silicate or sulfate of calcium, sodium and potassium on acid soils in connection with plant growth.

2. The acidity of the soils was reduced by the addition of carbonate, phosphate, biphosphate and silicate of calcium, sodium and potassium in the order mentioned, while sulfate did not make any reduction.

3. The hydrogen-ion concentration of the soil solution also was reduced by the addition of these salts, but the order of the reduction does not coincide with that observed in the case of the acidity.

4. The amount of aluminium dissolved out in the solution of potassium chloride from the soils after the addition of these salts agreed well with that of the acidity. The acidity seems, then, to be due to the amount of aluminium in the solution.

5. In their power to make soluble aluminium into insoluble, the salts rank in the following order: carbonate, phosphate, biphosphate and silicate. Sulfate not only lacks this power, but increases the amount of soluble aluminium. This order well coincides with that of the reduction of acidity by the salts.

6. The growth of barley was affected by the addition of the salts. A favorable effect was produced by phosphate, biphosphate, carbonate and silicate, in the order mentioned; while the unfavorable effect was caused by sulfate.

7. This order seems to agree with that of the salts in converting soluble aluminium into insoluble, except that phosphate and carbonate are inter-

changed. Hence the aluminium abundantly present in acid soils seems to be a very important factor causing inferior plant growth.

8. The superior effect of phosphate upon plant growth seems to be due to the great deficiency of phosphoric acid in this kind of soil.

9. Though the hydrogen-ion concentration of the soil solution also was reduced by the addition of the salts, it did not show any relation to the plant growth.

10. Thus, the inferior quality of the acid soil as a medium for plant growth is due in some measure at least, to the presence of soluble aluminium which is decidedly toxic, and to the deficiency of phosphoric acid. Hence the chemicals which supply phosphoric acid and cause the elimination of soluble aluminium seem to be the best agents for improving acid soil.

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PLATE 1

FIG. 1. Growth of barley on June 15 in Kutchan acid mineral soil showing the effect of the addition of calcium compounds.

Pot numbers	*Treatment*
0	Control
1	Calcium carbonate
2	Calcium phosphate
3	Calcium silicate
4	Calcium sulfate
5	Calcium biphosphate

FIG. 2. Growth of barley on June 15 in Kutchan acid mineral soil showing the effect of the addition of potassium compounds.

Pot numbers	*Treatment*
0	Control
6	Potassium carbonate
7	potassium phosphate
8	Potassium silicate
9	Potassium sulfate
10	Potassium biphosphate

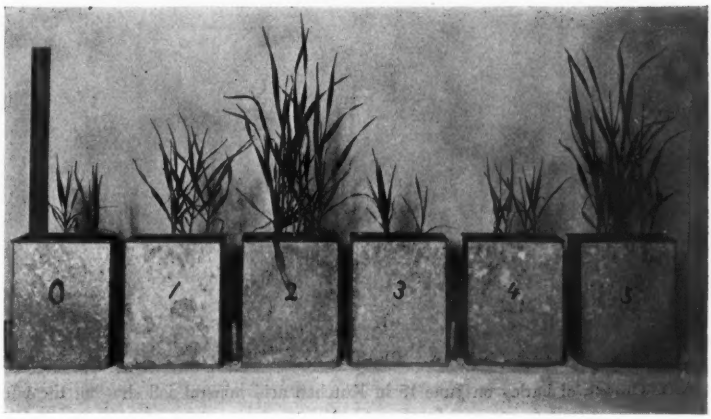

FIG. 1

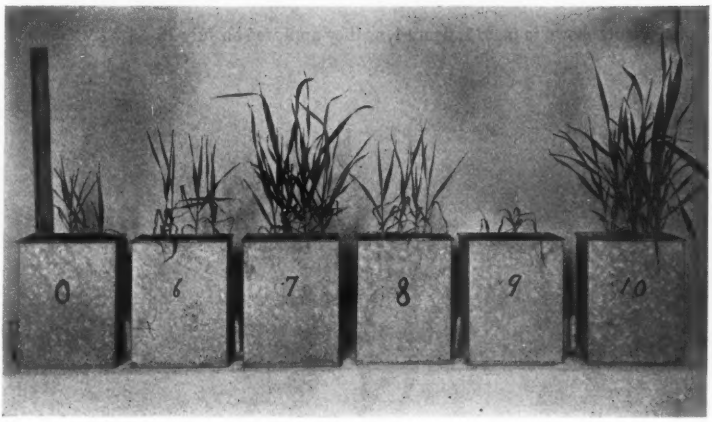

FIG. 2

PLATE 2

FIG. 1. Growth of barley on June 15 in Kutchan acid mineral soil showing the effect of the addition of sodium compounds.

Pot numbers	*Treatment*
0	Control
11	Sodium carbonate
12	Sodium phosphate
13	Sodium silicate
14	Sodium sulfate
15	Sodium biphosphate

FIG. 2. Plants shown in plate 1, figure 1, as they appeared on July 28.

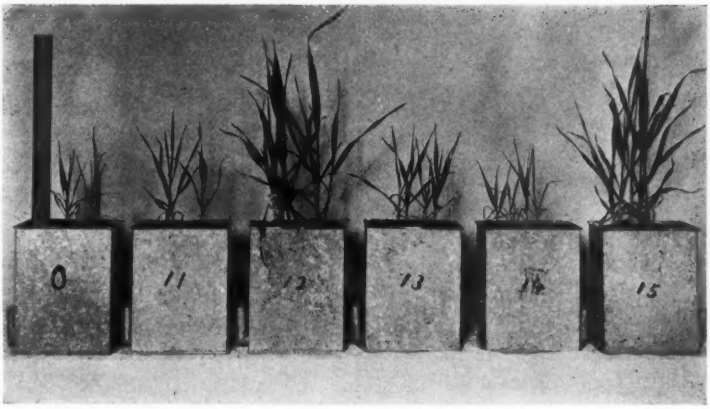

FIG. 1

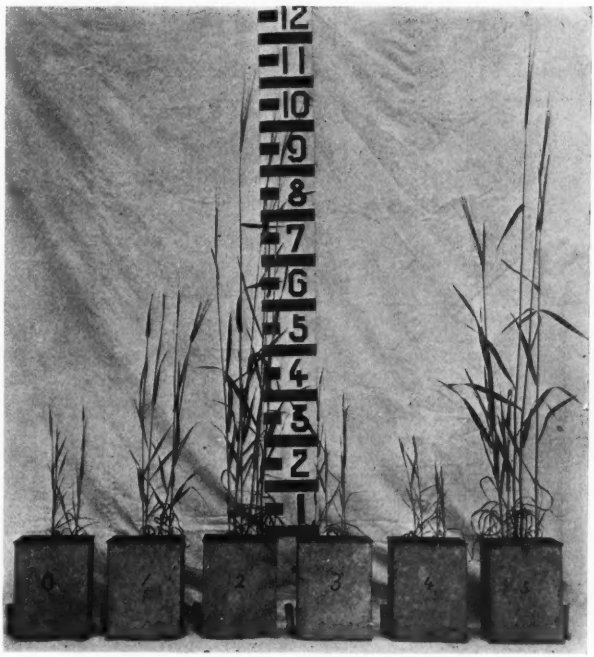

FIG. 2

PLATE 3

FIG. 1. Plants shown in plate 1, figure 2, as they appeared on July 28.
FIG. 2. Plants shown in plate 2, figure 1, as they appeared on July 28.

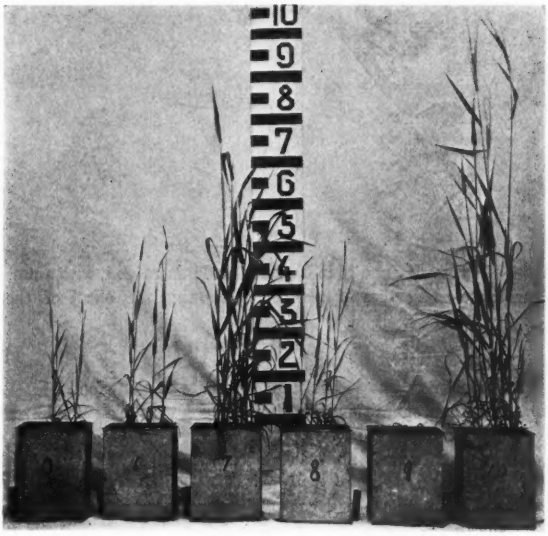

FIG. 1

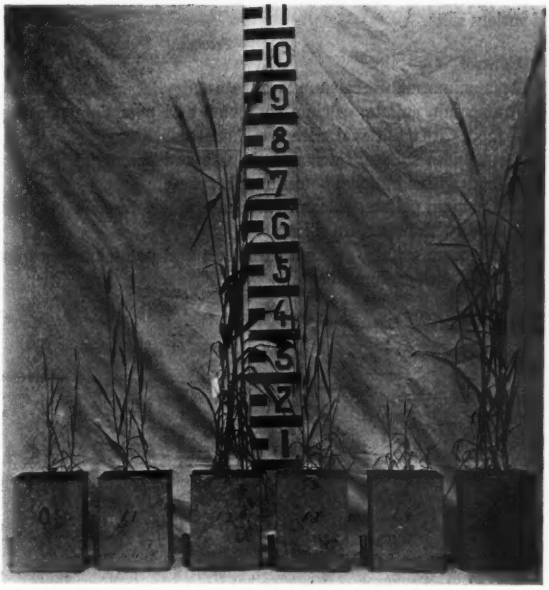

FIG. 2

PLATE 4

FIG. 1. Growth of barley on June 15 in Kutchan acid mineral soil, with ammonium sulfate and calcium carbonate as sources of plant-food, showing the effect of the addition of various salts.

Pot number	*Treatment*
0	Control
B1	Ammonium sulfate and calcium carbonate as plant-food
B2	Ammonium sulfate and calcium carbonate as plant-food; with additional calcium carbonate
B3	Ammonium sulfate and calcium carbonate as plant-food; with potassium phosphate
B4	Ammonium sulfate and calcium carbonate as plant-food; with potassium silicate
B5	Ammonium sulfate and calcium carbonate as plant-food; with sodium silicate

FIG. 2. Growth of barley on June 15 in Kutchan acid mineral soil, with ammonium sulfate, calcium carbonate and potassium phosphate as sources of plant-food, showing the effect of the addition of various salts.

Pot number	*Treatment*
0	Control
C1	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food
C2	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with additional calcium carbonate
C3	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with additional potassium phosphate
C4	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with potassium silicate
C5	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with sodium silicate

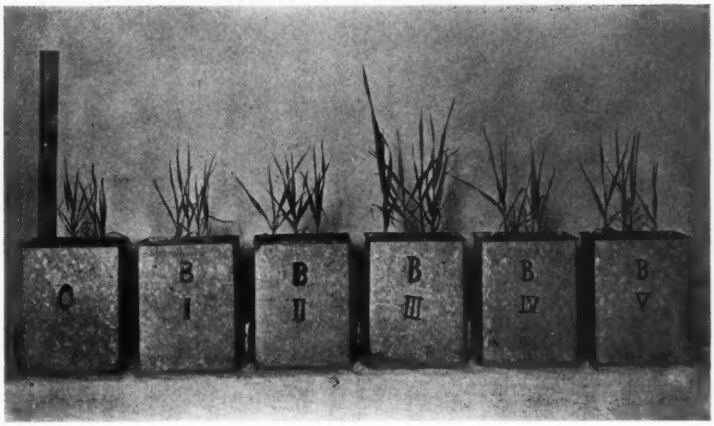

FIG. 1

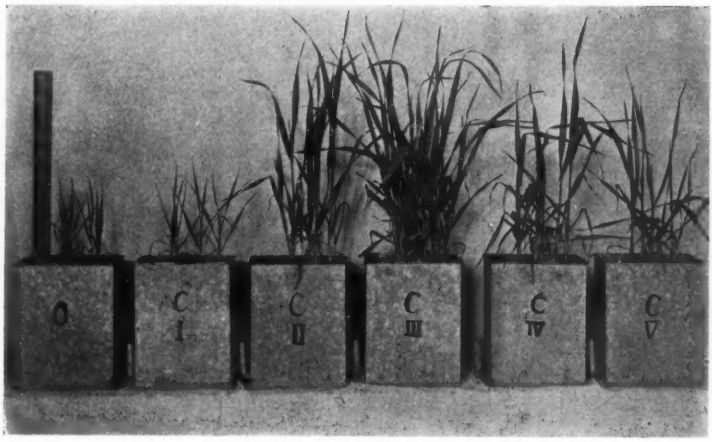

FIG. 2

PLATE 5

FIG. 1. Growth of barley on June 15 in Tayoro acid mineral soil, with ammonium sulfate and calcium carbonate as sources of plant-food, showing the effect of the addition of various salts.

Pot number	*Treatment*
0	Control
A1	Ammonium sulfate and calcium carbonate as plant-food
A2	Ammonium sulfate and calcium carbonate as plant-food; with additional carbonate
A3	Ammonium sulfate and calcium carbonate as plant-food; with potassium phosphate
A4	Ammonium sulfate and calcium carbonate as plant-food; with potassium silicate
A5	Ammonium sulfate and calcium carbonate as plant-food; with sodium silicate

FIG. 2. Growth of barley on June 15 in Tayoro acid mineral soil, with ammonium sulfate, calcium carbonate and potassium phosphate as sources of plant-food, showing the effect of the addition of various salts.

Pot number	*Treatment*
0	Control
B1	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food
B2	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with additional calcium carbonate
B3	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with additional potassium phosphate
B4	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with potassium silicate
B5	Ammonium sulfate, calcium carbonate and potassium phosphate as plant-food; with sodium silicate

FIG. 1

FIG. 2

PLATE 6

FIG. 1. Plants shown in plate 4, figure 1, as they appeared on July 28.
FIG. 2. Plants shown in plate 4, figure 2, as they appeared on July 28.

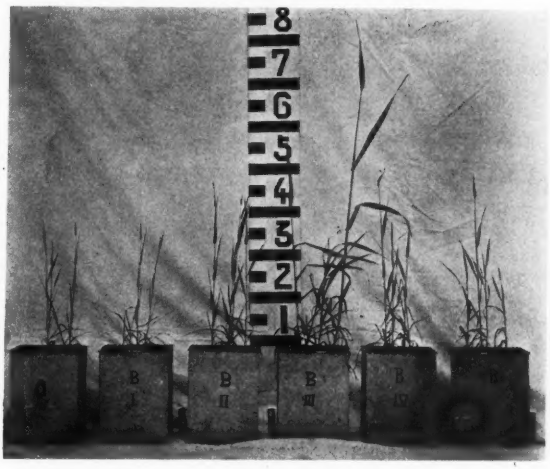
8
7
6
5
4
3
2
1
0
B I
B II
B III
B IV
B V

FIG. 1

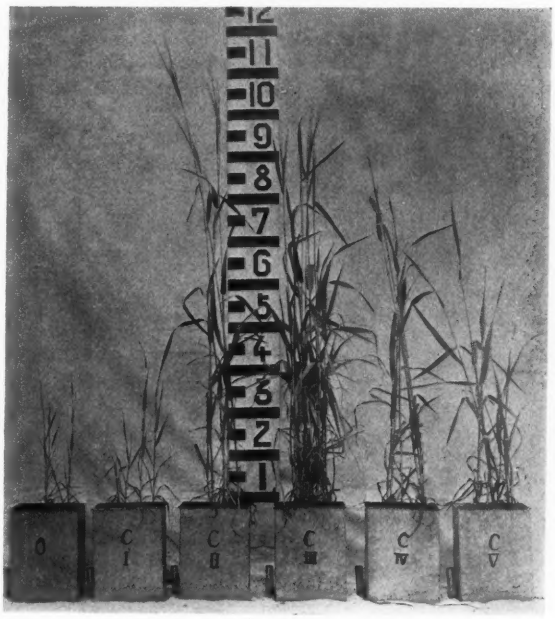
12
11
10
9
8
7
6
5
4
3
2
1
0
C I
C II
C III
C IV
C V

FIG. 2

PLATE 7

FIG. 1. Plants shown in plate 5, figure 1, as they appeared on July 28.
FIG. 2. Plants shown in plate 5, figure 2, as they appeared on July 28.

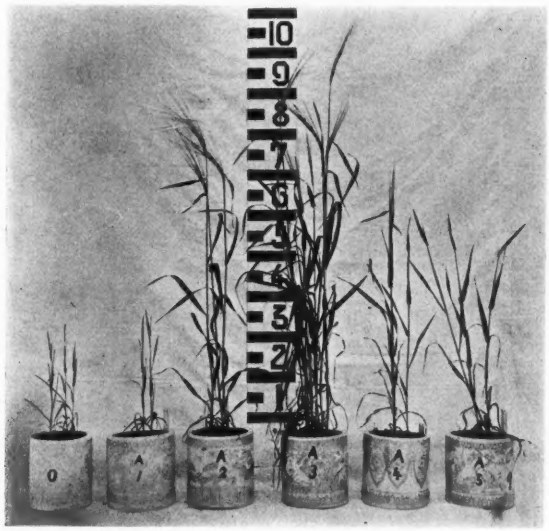

FIG. 1

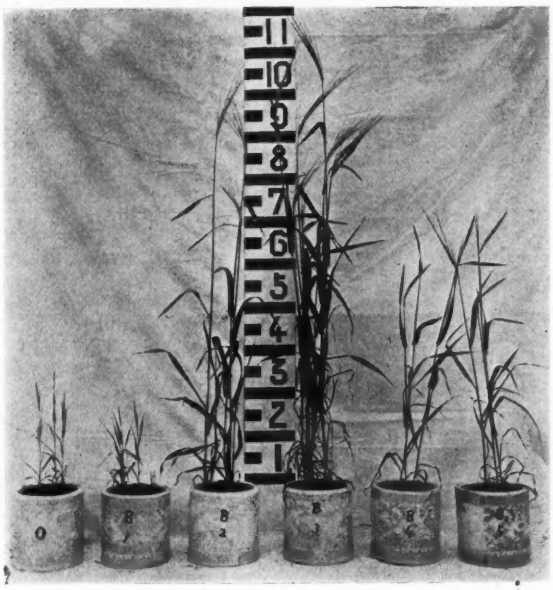

FIG. 2

THE AVAILABILITY OF NITROGEN IN PEAT

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University of California

Received for publication July 22, 1924

Large deposits of peat which are found at different points on the earth's surface have for many years rendered peat an object of considerable attention as a possible economic source of nitrogen as a fertilizing material and, incidentally also, of organic matter for soil treatment. The literature of the old agricultural chemistry and of soil science is replete with papers discussing experiments with peat or some economic factors connected with its use. In recent years another use for peat has been making demands which have enhanced its economic importance still more. We refer to the use of peat as filler material in commercial fertilizers. Both in the descriptions of some of the experiments to which we have just referred and in the commercial literature it has been repeatedly claimed that peat nitrogen may be regarded as a fairly good substitute for nitrogen in the better known commercial nitrogenous fertilizers. With this situation before us, we started an experiment to test out the availability of nitrogen in peat in a more or less natural condition and in a modified form due to special treatment. This experiment was concluded in 1919, but various circumstances have prevented us from publishing the results until now. In view of the circumstances to which we have alluded above and to the considerable commercial agitation prevalent during the last two or three years in favor of the use of peat for the improvement of the lawns of golf courses and similar places, it seems particularly opportune to discuss the actual results of experiment on this point. None of the other investigations which have a bearing on our experiment have regarded the problem in the way in which we have attacked it and the way in which we have interpreted the results. We append, however, a list of other papers which is of some interest in connection with the material furnished below.

THE PLAN OF OUR EXPERIMENT

Our aim in this investigation was to test the value of peat when applied to a soil which always responds to other nitrogenous fertilizers. Remembering also that the proteins in the peat might be easily hydrolyzed by steam under pressure and by treatment with acid, and possibly on an economical basis, we resolved to compare untreated peat with peat which had been treated

with sulfuric acid, and with peat which had been treated with sulfuric acid and steamed in the autoclave at 25 pounds pressure. The criteria upon which we decided to base our conclusions were the yields of barley in dry matter on the soils treated with the various forms of peat as compared with the yields of barley produced on the same soil which had received high grade nitrogenous fertilizers. The soil used in the experiment was Oakley blow sand which for many years has been shown by our laboratory to be highly responsive to nitrogenous fertilization of all kinds. Whenever peat was added to this soil it was added in quantities which would yield an amount of nitrogen equivalent to that found in an application of 200 pounds of nitrate of soda per acre. The computations made in these applications were based on the area of the exposed soil in the cultures and not on the weight thereof.

The peat which was used was derived from the surface layers of an area of peat land in the delta of the Sacramento and San Joaquin rivers. It was a brownish-black, apparently old material which could be readily reduced by grinding to a fairly fine condition. When it was applied to the soil it was very thoroughly mixed with the particles of sand therein. In its air-dried condition the peat contained 1.9 per cent of total nitrogen.

The cultures were grown in the usual glazed earthenware crocks of 2 gallons capacity, five barley plants per crock being planted and harvested. The treatments given the peat were as follows:

I. The peat was treated with sufficient concentrated sulfuric acid to just thoroughly wet it. It was allowed to remain in that condition over night. Enough water was then added to give the peat a content of 50 per cent of water.

II. Some of the acid-treated peat of treatment I. was then submitted to steam pressure in the autoclave at approximately 25 pounds pressure for 3 hours. It was made up to the same water content as the other peat. Five crocks with five barley plants each, as above indicated, were given to every treatment, which were as follows:

1. Oakley sand, no treatment.
2. Oakley sand to which peat had been added in an untreated condition and to an extent sufficient to add the nitrogen equivalent to that in 200 pounds of nitrate of soda per acre for the area in question.
3. Oakley sand to which acid-treated peat had been added on the same basis as regards nitrogen supply as in no. 2.
4. Oakley sand to which had been added steamed acid-treated peat at the same rate as regards nitrogen supply as in the other peat-treated soil.
5. Oakley sand plus nitrate of soda at the rate of 200 pounds per acre.
6. Oakley sand plus sulfate of ammonia at a rate supplying the same quantity of nitrogen as two hundred pounds of nitrate of soda to the acre.

The plants were grown for 100 days in the spring of the year and were harvested on May 21, 1919. The total dry matter was determined after drying for four days at 100°C. The yield from each crock was weighed as a mass.

THE RESULTS OF THE EXPERIMENT

Table 1 gives the results obtained with these cultures. It is perfectly clear from even a hasty examination of the dry weights of the barley obtained in the different cultures that an enormous difference obtains between the yields on the nitrate of soda and sulfate of ammonia treated soils and all the others. The nitrate of soda and sulfate of ammonia have induced a marked growth of barley plants as compared with that obtained on the control soils which remained untreated. On the other hand, the yields obtained on the soils treated with the three kinds of peat, prepared as described above, were apparently only slightly greater than those obtained on the control soils

TABLE 1

Dry weights of each group of plants

POT NUMBER	CONTROL		UNTREATED PEAT		ACID PEAT		STEAMED PEAT		$NaNO_3$		$(NH_4)_2SO_4$	
	Weight	Deviation	Weight	Deviation	Weight	Deviation	Weight	Deviation	Weight	Deviation	Weight	Deviation
	gm.		*gm.*		*gm.*		*gm.*		*gm.*		*gm.*	
1	1.340	0.340	2.390	0.460	1.950	0.058	1.250	0.512	5.440	0.246	5.230	0.416
2	2.260	0.616	2.300	0.370	1.850	0.158	1.770	0.008	4.810	0.384	5.770	0.124
3	2.000	0.356	1.700	0.230	1.450	0.558	1.090	0.672	4.750	0.444	6.030	0.384
4	1.670	0.026	1.600	0.330	1.590	0.418	1.930	0.168	5.870	0.676	5.520	0.126
5	0.950	0.694	1.660	0.270	3.200	1.192	2.770	1.008	5.100	0.094	5.680	0.034
Mean	1.644	0.399	1.930	0.332	2.008	0.477	1.762	0.474	5.194	0.369	5.646	0.217
Increase over control			17.4%		22.2%		7.2%		216.4%		243.3%	
σ	0.465		0.339		0.621		0.590		0.417		0.265	
Probable error	±0.140		±0.087		±0.187		±0.178		±0.126		±0.080	

which received no treatment. In order to introduce another factor safeguarding the significance of our results more than other experiments on this subject have been safeguarded, we treated our data, so far as such meager replications would allow, by the statistical method. Table 1 indicates not only the actual yield obtained on the several cultures in every series but also gives the deviations from the mean and the probable error involved in all of them.

Before discussing the data from the point of view of the statistical treatment of them, we may point out that the yields of replicate cultures with any given treatment are highly variable. This is particularly true with the cultures of the control soil and of the peat-treated soils. It will be remembered that the treatment of the peat prior to its use in connection with the soils of the experiment could not have produced great abnormalities in the soil, since only a very small quantity of peat was necessary, relatively speaking, to supply the same amount of nitrogen as was contained in a 200-pound

application of nitrate of soda per acre. This, in fact, is supported by the evidence that the acid-treated peat gave slightly superior results to the untreated peat, and both of them apparently gave better results than the control soils. The reason for the poor results obtained with the steamed peat

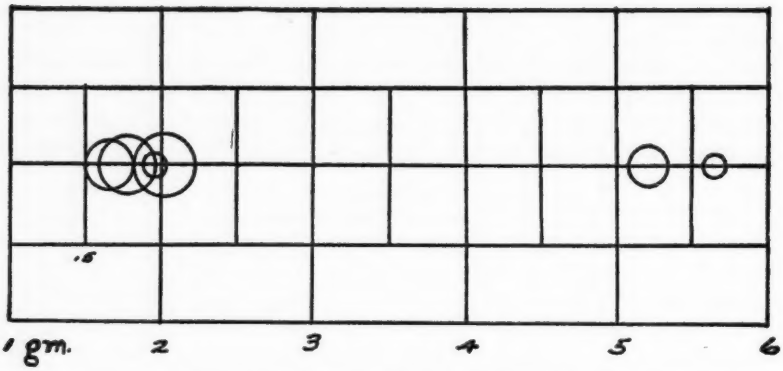

FIG. 1. GRAPHICAL COMPARISON OF ACTUAL YIELDS OF SERIES, MAKING ALLOWANCE FOR THE PROBABLE EXPERIMENTAL ERROR

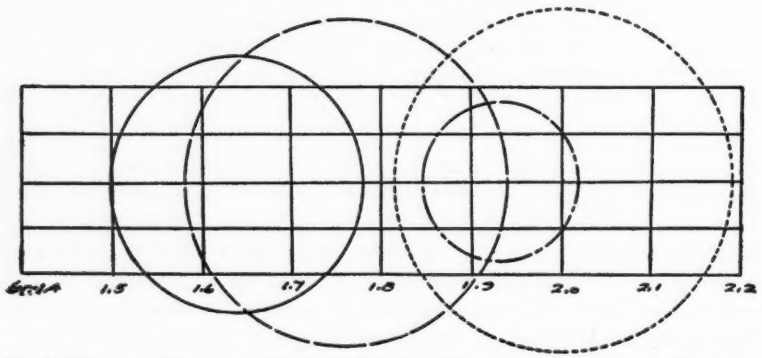

FIG. 2. ENLARGED PORTION OF FIGURE 1, SHOWING RELATIONS OF PEATS AND CONTROL

——————Control
—— ——Steamed Peat
—— - ——Untreated Peat
– – – – – – –Acid Peat

probably lies in the fact that the highly available nitrogen compounds contained in the peat were destroyed by steaming under pressure.

These observations, however, are of little significance when we come to make a statistical study of the data in question. In our statistical studies the reliability of each group of determinations is expressed by the probable

error of the group. This is indicated in table 1. This figure is of such magnitude that the probability of making an error greater than it is equal to probability of making an error less than it, both probabilities, therefore, being one-half. When the data are treated in this fashion it is possible to give a very interesting graphic illustration of their significance. This is given in figures 1 and 2. Figure 2 is particularly illuminating with regard to the problem in hand. The centers of the circles in the figure represent the means of each series. The radii are the probable errors. If any one of the circles representing treated soils overlaps that representing the control soil, the apparent increase in production of the treated series as judged by arithmetical averages, is not significant but falls within the limits of probable error. If, on the other hand, the circles do not overlap, the increase or decrease noted is outside the limits of experimental error and is, therefore, significant. When judged on this basis, the steamed peat treatment gives no increase over the control soils, the acid peat shows an increase of 0.037 gm. per series of five crocks, and the untreated peat a similar gain of 0.059 gm. While both of these figures are significant, they have very little practical interest inasmuch as they represent differences from the control which are too slight to be of any moment in connection with the use of peat for agricultural or commercial purposes. On the other hand, it becomes perfectly clear that the circles drawn on the basis of the sodium nitrate and sulfate of ammonium cultures as given in figure 1, are clearly far outside the reaches of the circle representing the control soil. The differences between the two are, therefore, highly significant.

Two conclusions follow clearly from the foregoing data and discussions. The first is that it makes little difference how peat is treated within economic limits as regards its value as a nitrogen supplying material from the point of view of available nitrogen. Second, no matter how peat is treated, or if it remains untreated, it still is far inferior as a source of available nitrogen to the high grade commercial fertilizer. Third, the intrinsic value of peat as a source of available nitrogen may be said to be almost nil on such a soil as the Oakley sand which responds, however, readily to other nitrogen fertilizers.

CONCLUSION

From the experiment described above, it may be asserted that peat untreated or treated with acid and with acid plus steam under pressure, is of practically no value as a source of available nitrogen when results from particular experiments carried on for this purpose are properly studied.

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INFLUENCE OF SULFUR OXIDATION ON SOLUBILITY OF SOIL MINERALS

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Received for publication July 23, 1924

In the semi-arid section of Oregon sulfur is giving excellent results as a fertilizer, especially when used on legumes. According to Powers (4) there are at least 100,000 acres of alfalfa land in Oregon on which the yield can be materially and profitably increased by systematic sulfuring. The increased yield, usually very large, is caused by the lightest applications of sulfur, even as little as 50 pounds per acre yearly. The reason for the phenomenal stimulation in yield is not well understood. Perhaps the sulfur may serve as plant food directly, or bacterial action may be stimulated, plant food may be thrown into solution or other factors may cause the increase.

During the past year, pot studies were started in the laboratory to determine the effect on solubility of essential elements of plant-food, including potassium, phosphorus, and calcium, recognizing that herein might lie in part at least, an explanation.

Two types of soil were used, the one an arid soil called Deschutes sandy loam which is nearly neutral, and the other a soil from the humid section called Willamette silt Loam which is a typical good valley soil but quite acid in reaction. The soils were selected as being expecially adapted to respond to sulfur studies. They were also known to respond to application of potash-bearing fertilizer.

Besides a check, four different rates of sulfur treatment were used, 100, 500, 2500, and 12,500 pounds per 2,000,000 pounds of soils. The pots were maintained at about the optimum moisture content and were sampled three times at intervals of 4, 6 and 9 months. After each sampling, nitrates, water soluble potassium, phosphorus, calcium, and sulfates were determined.

Colormetric and turbidity methods were used throughout the work, following the procedures with some modifications, outlined by the Bureau of Soils (5). While not entirely satisfactory the methods have the advantage of adaptation to small quantities, and suitability for rapid work. In much of this work differences have been sufficiently marked that greater accuracy would hardly be significant.

The results are shown in table 1.

Soluble nitrates determined at each sampling showed that the heavy applications of sulfur depressed nitrification very decidedly at first but to a less extent as time went on. With an application such as is practical under field conditions there was no appreciable depression of nitrification.

The effect of the sulfur oxidation upon the increase in water soluble calcium was very striking. The soluble calcium was increased several fold with the heavier applications and even the lightest application of 100 pounds of sulfur produced an appreciable increase in the soluble calcium. Since legumes and especially alfalfa are heavy lime feeders, this no doubt may be a contributing

TABLE 1

Water soluble plant food in soil treated with sulfur

SULFUR TREATMENTS PER ACRE	N SAMPLINGS			K SAMPLINGS			PO_4 SAMPLINGS			Ca SAMPLINGS			SO_4 SAMPLINGS		
	1*	2*	3*	1	2	3	1	2	3	1	2	3	1	2	3
Deschutes sandy loam															
pounds															
None	17	10	30	15	14	11	49	50	46	83	67	56	Tr.	15	40
100	18	11	40	18	16	21	47	43	48	118	92	70	125	143	114
500	13	9	26	36	35	40	32	40	38	143	196	208	500	666	714
2,500	Tr.	2	9	67	54	54	23	31	35	200	370	385	1800	1667	2222
12,500	Tr.	2	4	84	88	98	7	13	27	286	556	833	3000	4167	5555
Willamette silt loam soil (Gouley Experiment Field, Salem)															
None	31	22	21	12	9	11	38	22	28	64	59	66	50	49	53
100	40	22	19	9	9	10	39	20	20	88	92	130	75	137	133
500	33	21	19	15	13	15	31	13	16	125	172	250	135	237	444
2,500	9½	7	9	20	21	29	6	9	9	188	298	769	325	1357	2000
12,500	Tr.	6	5	23	32	48	Tr.	8	18	232	543	1333	400	2853	4000

* 1 Indicates sampling after 4 months; 2, after six months; and 3, after 9 months.

cause for the big response of alfalfa to light sulfur applications. The continued use of sulfur may cause increased loss of lime by leaching due to the great increase in solubility unless precautions are observed.

Soluble potassium was greatly increased on both soils by the heavier applications. The oxidation of the sulfur to produce acid amounted virtually to an acid extraction of the soil, with a very dilute acid. The effect was more marked on the Deschutes soil. Since arid soils are less deeply weathered, and contain minerals rich in plant food, this result is logical. The arid soils also being generally alkaline, and changed to acid condition by the oxidation of the sulfur, should give up more plant food to a water extract than would humid soils. Increased solubility of potassium may be desirable under some conditions but undesirable under others. When potassium is deficient and

becomes a limiting factor in crop production, the increased solubility should show in increased crop yields. Land left barren, however, would be more likely to lose potassium by leaching after a treatment with sulfur. The general effect should be much the same as from the application of a soluble potassium fertilizer.

The effect of the sulfur on water soluble phosphate was the reverse of the effect upon potassium. The effect was more marked on the Willamette soil, which was made highly acid, since it was already rather acid at the start. This seems to corroborate the oft noted results that acid soils are in need of phosphate fertilizers. The explanation for the reduced amount of soluble phosphate may lie in the fact that increased solubility of the calcium causes the phosphate to be rendered insoluble as tri-calcium phosphate. In any event the solution and reprecipitation of the phosphate as tri-calcium phosphate may not render the phosphorus less available to crops than it was in the original form. If the preponderance of soluble calcium prevents the phosphate from being taken up by iron and aluminum the result may be decidedly beneficial. The depressing effect of the sulfur on the solubility of the phosphate seemed to become less marked at the last sampling. Perhaps in time a redistribution and precipitation of the phosphate may occur, and the depressing effect disappear. On soils, too, with less soluble calcium the effect of depressing soluble phosphate might disappear. This reciprocal relation of soluble calcium relative to phosphate has been noted by other workers (1).

The amount of water soluble sulfates obtained is a rough measure of the rate of oxidation of the sulfur. The Deschutes soil apparently had a low water soluble sulfate content, sufficiently low perhaps that sulfur may become a limiting element of plant food. How general the condition is cannot be stated. The Deschutes soil oxidized sulfur more rapidly, undoubtedly because of its more open structure and partly, perhaps, because of its alkaline or neutral reaction at the beginning. Though there was an increase in the amount of oxidized sulfur with each successive sampling, in no case was nearly all the sulfur oxidized. Though it was four months before samplings were made oxidation probably started almost immediately. Tumbler studies with another soil, Hanford gravelly sandy loam, treated at the rate of 2500 pounds of sulfur per 2,000,000 pounds of soil, showed 6, 13, 23, 47 and 57 per cent oxidized after 1, 2, 3, 4, and 8 weeks respectively. Oregon soils in general according to Halversen and Bollen (2) have an active sulfur oxidizing soil flora.

The oxidation of the larger application of sulfur caused an appreciable increase in the acidity of the soils. The Deschutes soil which was nearly neutral at the start was made very slightly acid at the first sampling with 500 pounds of sulfur. The higher application caused decided acidity. The Willamette soil was made more acid but the acidity of the original soil was so great that the Truog lead acetate test did not give an easily distinguishable difference.

Hydrogen-ion concentrations were determined on both soils at the second sampling only. Results are shown in table 2. The determinations for total lime requirement were made also on the last sampling, and are shown below.

Only the very heavy applications on the Deschutes soil brought the pH value to marked acidity. On the other soil even the lighter applications caused a considerable increase in the hydrogen-ion concentration. Since sulfuric is a very strong acid, a little of it, unless neutralized by some reaction with the soil should produce a marked change in the pH value. The Deschutes soil has a high calcium content and probably contained a number of salts which caused a neutralization of the acid.

The amount of lime as calcium carbonate required to neutralize the acidity is shown for the last sampling as determined by the Jones method (3). The results show that no lime requirement was produced on the Deschutes soil

TABLE 2

Table showing pH values for soils at second sampling and also lime requirement by the Jones method (third sampling)

SULFUR TREATMENT	DESCHUTES SOIL		WILLAMETTE SOIL	
	Lime requirement	pH value	Lime requirement	pH values
pounds	*tons*		*tons*	
0	0	7.0	2.24	6.4
100	0	6.8	2.55	5.4
500	0.32	6.5	2.65	4.6
2,500	1.13	6.3	4.69	4.4
12,500	4.69	4.1	7.54	3.9

with less than 500 pounds of sulfur per acre. On the other soil each application of sulfur increased the lime requirement somewhat. The lime requirements in general ran parallel with the changes in pH values. Alfalfa does best in nutrient solutions having slightly acid reaction, or about pH 6.0. While this plant flourishes in soils of neutral reaction, yet a possible beneficial effect from sulfur applications on arid soil may come about through slight increase in hydrogen-ion concentration.

The physical effect of the sulfur after it was oxidized to the sulfate was very noticeable. The colloidal material which made it very difficult to obtain a clear filtrate was flocculated. The effect was very noticeable for the applications above 500 pounds per acre. The flocculating effect of the sulfate has special significance on heavy soils and on soils where flocculation is necessary in order to wash out harmful accumulations of alkali. In this respect sulfur functions in the same way in the end as an application of gypsum. Sulfur is in three times as concentrated a form as to bulk, and where long freight shipments are necessary may be more economical than gypsum for that reason.

CONCLUSION

The oxidation of sulfur applied to two widely different soils, one representative of arid and the other of humid conditions, caused a decided increase in the water soluble calcium and potassium, but reduced the amount of water soluble phosphorus.

Even the lighter applications produced an increase in acidity, and long continued use of sulfur on soils already slightly acid, would no doubt cause some injury due to acidity, unless neutralized by the use of lime.

The flocculating effect of the oxidized sulfur may be of considerable value under certain conditions.

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THE INFLUENCE OF NITRIFYING BACTERIA ON THE GROWTH OF BARLEY[1]

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Received for publication July 25, 1924

The beneficial effect of nitrates for plants is well known, and yet direct evidence, of increased growth of the higher plant while nitrification is in progress is not easy to demonstrate. Owing to the great number of factors involved in the growth of plants, it is sometimes difficult to measure the effect of any one factor. Provided the conditions are proper, nitrification should bring about an increase in the growth of the plant similar to that noted with the nodule bacteria of legumes.

The present report was undertaken for the purpose of measuring the effect of nitrification on growing plants. This work is a part of a major study on nitrification, certain phases of whichwere presented in 1919 and 1921 (1, 2). This paper presents data on the effect of pure cultures of nitrifying bacteria on the growth of barley in sand cultures.

EXPERIMENTAL

The tests were made in 2-gallon earthenware jars containing pure washed sand and a nutrient solution which contained nitrogen in the form of ammonium sulfate. Twelve kilos of sand and 15 gm. of limestone were thoroughly mixed and placed in each jar. These were then sterilized in the autoclave for five hours, and when cool, 20 cc. of the modified Shive's nutrient solution were added. Pure cultures from washed agar of the nitrifying bacteria, *nitrosomonas* and *nitrobacter* were added at the same time as the nutrient solution. The plan is given below.

Group A. Jars 1 and 2, controls, no nitrogen.
Group B. Jars 3 and 4, controls, with nitrogen as ammonium sulfate.
Group C. Jars 5 and 6, nitrifiers with nitrogen as ammonium sulfate.

In the modified Shive's nutrient solution, the calcium nitrate was replaced with an equivalent amount of nitrogen in the form of sulfate of ammonia. The moisture content of sand cultures was made up to two-thirds saturation and kept the same throughout the experiment.

[1] Published with the approval of the Director of the Wisconsin Agricultural Experiment Station.

Two weeks later each jar was planted to ten barley seeds which had been treated to remove the bacteria. The plants were thinned to six seedlings per jar. During the growing period, plant food was added from time to time according to the plan. In all, seven applications of the modified plant food were made. To prevent contamination, the jars were kept in a special greenhouse well separated from other plants and only sterilized water used.

The barley grew rapidly except in those jars without nitrogen. At the end of 102 days the plants were photographed and then harvested. The average green weights of the duplicate jars were as follows:

	grams
Group A. Control, no nitrogen	1.5
Group B. Control with ammonium sulfate	66.5
Group C. Nitrifiers with ammonium sulfate	116.0

The results are striking; the green weights of the plants without nitrifying bacteria are distinctly inferior to those with the nitrifiers. Plate I shows the marked difference in comparative growth of the barley under the different conditions.

A year later a similar experiment was repeated with a slight change. Group A, the controls without nitrogen, were omitted. With this exception the same plan was followed.

Pure cultures of the nitrifying bacteria were added two weeks before planting. At various intervals during the growing period comparisons were made of the plants with nitrifiers and plants without. The presence and the absence of the nitrifying bacteria in the control jars as well as the treated was determined by means of qualitative tests.

It was found that within ten days after planting, the jars receiving the nitrifiers showed a more vigorous growth than those without bacteria. As the plants developed this difference in favor of the inoculated sand cultures became more noticeable. When one month old the plants with nitrifiers were 4 to 5 inches taller than the others and showed much more tillering. Here as in the previous experiment, there were seven applications of plant food, of 20 cc. nutrient solution per jar.

During the growth of the barley of this second test, samples of sand were removed from the jars and tested for nitrates. The samples from jars with ammonium sulfate but no nitrifiers added always gave a negative reaction for nitrates while those with nitrifiers added gave a strong positive test for nitrates.

When 80 days old, the plants were photographed and then harvested. Plate 2 shows the striking difference between the inoculated and uninoculated plants. The average green and dry weights and also total nitrogen content follow:

	WEIGHT OF BARLEY		TOTAL NITROGEN IN BARLEY
	Green	Dry	
	gm.	gm.	gm.
A. Without nitrifiers added	145.0	30.0	0.66
B. With nitrifiers added	258.0	52.8	0.78

The differences in growth and in total nitrogen are clearly in favor of the jars with nitrifying bacteria present. The yield of barley in the jars to which the nitrifiers were added was almost twice as much as that in the jars without the culture of nitrifying bacteria. Under the conditions outlined in these tests it is possible to show by means of plant growth the beneficial effect of the nitrifying bacteria.

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PLATE 1

BARLEY IN SAND CULTURES SHOWING EFFECT OF SULFATE OF AMMONIA AND NITRIFICATION

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BARLEY
WITHOUT
NITROGEN
BARLEY
WITH
SULPHATE OF AMMONIA
BARLEY
WITH
SULPHATE OF AMMONIA
AND
NITRIFYING BACTERIA

PLATE 2

EFFECT OF NITRIFICATION ON GROWING BARLEY

METHODS OF STUDYING THE STRENGTH OF SOIL ACIDS[1]

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Received for publication August 11, 1924

The acid properties of a soil depend upon the amount and strength of the acids in the soil. The importance of these two factors, quantity and intensity, in soil acidity has been recognized by many investigators. However, more work has been devoted to a study of the quantity factor than to a study of the intensity factor. The purpose of this investigation was to study and compare methods for measuring the intensity factor in soil acidity.

It is possible to classify soil acidity methods with respect to the influence the quantity and intensity factors have on the results obtained by the method. Classified on this basis the methods would be divided into three groups: first, those which measure the amount of soil acids; second, those which indicate the strength of the soil acids; and third, methods which are influenced by both the amount and the strength of the acids. The first group would include the Veitch, Tacke, McIntire, and various titration methods. The third group includes the Hopkins, Jones, Truog, and a number of other soil acidity tests. Most of the methods in these two groups have been studied and compared by different investigators.

Methods for studying the strength of soil acids have received less attention than the methods of the other two classes. The avidity method of Truog (9) is probably the only one that has been advanced for the specific purpose of studying the strength of the soil acids. Stevenson (8) has used the Tacke method in a study of the activity of soil acids but it is not as well adapted to the purpose as some other methods.

The hydrogen-ion concentration of soil suspensions and extracts indicates the intensity of the acidity of these suspensions and extracts. However, Salter and Morgan (6) and Bradfield (1) have shown that the hydrogen-ion concentration of soil suspensions is influenced by the soil-water ratio. The same condition has been found to be true for the sugar inversion method (5, 6). Consequently these two methods as ordinarily used are not well adapted to the study of the strength of the soil acids. When the procedure is modified so that the amount of soil acid is a constant the two methods are very satisfactory for a study of the strength of soil acids.

[1] Published with the permission of the Director of the Alabama Agricultural Experiment Station.

EXPERIMENTAL

Twenty-five soils representing fifteen soil types were used in this work. The soils were air-dried and passed through a 20-mesh sieve. They were then ground with a rubber pestle to break up the granular structure without grinding the coarse particles.

The strength of the soil acids was determined by three methods: viz., hydrogen-ion concentration, sugar inversion, and by the Truog avidity method. With each of these methods it is necessary to know the amount of acid in the various soils. This was determined by Truog's active acidity method (9) since it is a part of his avidity method. Then for the hydrogen-ion and sugar inversion methods the amount of the different soils was varied so that the amount of acid present would be the same for all soils. In the Truog avidity method the amount of reagent is varied so that it is just equivalent to the amount of soil acid. Hence, all differences obtained by the methods may be attributed to differences in the strength of the acids of the various soils.

The sugar inverting power of soils seems to depend on the amount and strength of the soil acids. Rice and Osugi (5) and Salter and Morgan (6) have shown the influence of the soil-water ratio on sugar inversion. In the determinations reported in this paper the amount of soil was varied so that all samples would contain the same amount of acid. In the case of soils with a high lime requirement a relatively small amount of soil was used. For example, with soil 203, having a lime requirement 15.60 tons per acre, 3.85 gm. of soil was used; and with soil 54, having a lime requirement of 1.15 tons per acre, 52.20 gm. of soil was used. In each case the amount of soil had a lime requirement of 0.06 gm. of calcium carbonate. Therefore, any difference in the amount of sugar inverted by the soils could hardly be attributed to differences in the amount of acid but would apparently be due to differences in the strength of the acid.

The soil was placed in a 300-cc. Erlenmeyer flask with 100 cc. of a 5 per cent sucrose solution and the flask fitted with a reflux condenser. The flasks were then placed in a large thermostat which was maintained at a temperature of 79° to 81°C. for 3 hours. Each flask was shaken by hand every fifteen minutes. After the three-hour period the flasks were cooled, the suspension filtered by suction, and the extract titrated, using Benedict's solution. The results are expressed as milligrams of sucrose inverted by the soil acid.

The results of Salter and Morgan (6) and Bradfield (1) show that the amount of soil acid in a suspension materially influences the hydrogen-ion concentration. Hence, it seemed desirable in this work to vary the amount of soil added to a given quantity of water so that the same amount of acid was present in all cases. Since the results were to be compared with the results of the sugar inversion method the same quantity of soil and water was used for the hydrogen-ion determinations as was used in the sugar inversion method. The measurements were made by the electrometric method, using a Leeds and

Northrup hydrogen-ion potentiometer. The hydrogen-ion concentration was determined before and after heating at 79° to 81°C. for three hours. Heating at this temperature had very little effect on the hydrogen-ion concentration. This is in agreement with the results of Sharp and Hoagland (7). The results in table 1 were obtained after heating and represent the average of closely agreeing duplicate determinations. In most cases duplicates agreed to within pH 0.05.

TABLE 1

The strength of soil acids as indicated by the Truog method, sugar inversion, and the concentration of hydrogen-ions

SOIL NUMBER	SOIL TYPE	LIME REQUIREMENT	AVIDITY BY TRUOG METHOD	SUCROSE INVERTED	HYDROGEN-ION CONCENTRATION
		tons $CaCO_3$		*mgm.*	*pH*
48	Greenville sandy loam	2.30	30.9	12.5	6.48
54	Greenville sandy loam	1.15	38.7	22.8	6.25
44	Hagerstown silt loam	2.55	48.6	14.4	5.88
59	Norfolk sandy loam	1.20	49.7	40.4	6.15
61	Orangeburg fine sandy loam	1.75	53.0	49.6	5.61
186	Ruston fine sandy loam	3.55	62.7	24.3	5.73
52	Clarksville silt loam	3.25	62.7	45.2	5.45
60	Ruston fine sandy loam	2.60	67.9	44.4	5.42
104	Norfolk sandy loam	2.40	69.5	59.3	5.21
43	Clarksville silt loam	3.15	72.8	69.1	5.33
101	Louisa fine sandy loam	2.75	80.8	64.6	5.23
56	Greenville sandy loam	3.70	84.8	117.2	5.31
666	Norfolk fine sandy loam	7.50	85.2	68.4	5.23
50	DeKalb fine sandy loam	2.85	85.5	86.6	5.21
100	Orangeburg sandy loam	3.70	85.6	66.8	5.51
45	Holston silt loam	4.50	87.4	59.3	5.28
97	Louisa fine sandy loam	2.95	88.5	88.6	5.16
204	Greenville sandy loam	4.90	98.8	60.0	5.28
72	Clarksville silt loam	2.65	102.0	99.0	5.20
78	Norfolk fine sandy loam	8.50	110.0	155.1	4.86
77	Susquehanna fine sandy loam	3.20	110.0	89.0	5.05
47	Oktibbeha clay loam	3.00	158.0	188.7	4.91
151	Clarksville silt loam	3.50	210.0	242.0	4.83
197	Susquehanna clay (subsoil)	11.50	432.0	293.6	4.93
203	Susquehanna clay (subsoil)	15.60	472.0	278.5	4.82

In the Truog avidity method equivalent amounts of soil acid and acetic acid are allowed to compete for a quantity of base just sufficient to neutralize one of the acids. The distribution of the base is determined by titration. The procedure used was the same as that recommended by Truog except for slight modifications to render it more accurate. The time allowed for filtering was made constant for all soils, 2 minutes. The amount of extract recovered from different soils varied slightly depending on the texture. Therefore, a 100-cc. aliquot was titrated and the acidity of the 150-cc. was calculated. It should

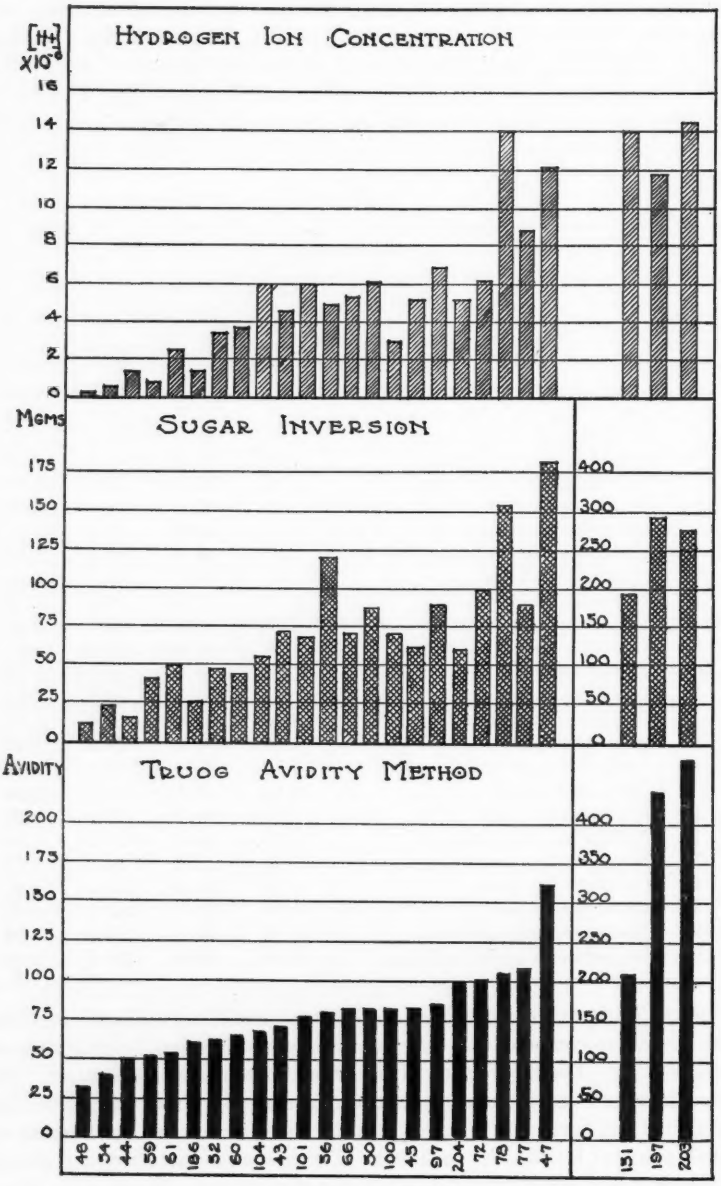

FIG. 1. THE STRENGTH OF THE SOIL ACIDS AS INDICATED BY THE HYDROGEN-ION CONCENTRATION, SUGAR INVERSION, AND THE TRUOG AVIDITY METHOD

be noted that in this method the amount of potassium acetate added to the soil is exactly equivalent to the acid in the 50-gram soil sample used in the determination.

The results obtained by the three methods are given in table 1. The third column of the table gives the amount of acid in the soil, expressed as tons $CaCO_3$ per acre, as determined by Truog's method for active acidity. The soils are arranged in the order of their avidity according to the Truog method. The hydrogen-ion concentration is given as pH values. The same results are shown graphically in figure 1.

There are several facts of interest regarding the correlation between the results of the three methods. The avidity of the soil acids varied from 30.9 to 472 but sixteen of the twenty-five soils had an avidity between 40 and 100. The amounts of sugar inverted by the soils varied from 12.5 mgm. to 293.6 mgm. and fifteen of the twenty-five soils inverted between 40 and 100 mgm. of sucrose. The hydrogen-ion concentration varied from pH 6.48 to pH 4.82. Seventeen soils gave a pH value between 5.0 and 6.0. These results and a study of figure 1 show that there is a good correlation between the results of the three methods. The coefficient of correlation between the results of the methods was calculated. The coefficients are as follows:

1. Truog avidity and sugar inversion methods ..... 0.899 ± 0.025
2. Truog avidity method and hydrogen-ion concentration ..... 0.789 ± 0.050
3. Sugar inversion method and hydrogen-ion concentration ..... 0.817 ± 0.045

All of these coefficients are high, the best correlation being between the sugar inversion and Truog avidity methods.

The fact that the three methods correlate as they do is of special interest when we consider that the principles on which the methods are based differ. Truog's method, based on the competition of acids for potassium, is designed to measure the strength of the relatively insoluble soil acids. The hydrogen-ion concentration is determined by the acids that are in solution and dissociated. The amount of sugar inverted probably depends on the acidity of the solid phase as well as upon the hydrogen-ion concentration of the solution (3, 4). Thus one method is influenced by the acidity of the solid phase, another by the acidity of the solid and liquid phases, and the third by the acidity of the liquid phase only. Since the three methods give similar results with twenty-five soils it is apparent that there must be a close relationship between the acidity of the solid phase and the acidity of the soil solution or extract. This relationship may be explained by the assumption that the acids of the solid phase undergo hydrolysis producing hydrogen ions, and that the extent of hydrolysis is determined by the strength of the acids. No doubt other factors such as the salt content of the solution affects hydrolysis and the hydrogen-ion concentration of soil suspensions. It is probable that if that factor had been constant for the soils used in this study the correlation of the results of the three methods would have been even better.

In the preceding discussion the factors affecting the different methods have been assumed without giving definite proof that they were the only or principal factors involved. There is a little or no doubt regarding the factors influencing the Truog method or the hydrogen-ion concentration. However, there is some question as to the factors involved in the hydrolysis of sucrose by suspensions of acid soils. A number of investigators have studied the inversion of cane sugar by acid soils with some conflicting results. However, the following facts seem to be well established:

A. Only acid soils, those having a pH value less than 7.0, invert more than very small amounts of sugar (4, 7).

B. Water extracts of acid soils invert sugar (7).

C. Suspensions of acid soils invert considerably more sugar than water extracts of the same soil (5, 7).

D. Increasing the amount of the solid phase in the suspension increases the rate of inversion (5, 6).

Several explanations have been advanced to explain the influence of the solid phase on inversion. Rice and Osugi (5), Osugi (3), and Parker and Bryan (4) attribute the influence directly to the acidity of the acid silicates in the soil. Sharp and Hoagland (7) and Osugi (3) have suggested that it may be due to a higher concentration of hydrogen-ions at the surface of the soil particles than in the solution. Parker and Bryan offered some data which they interpreted as indicating that there was not a concentration of hydrogen ions at the surface of the soil particles. Sharp and Hoagland also suggested that the effect of the solid phase might be due to its stabilizing influence on the reaction of the solution. Salter and Morgan attribute the effect of the amount of the solid phase to the differences in the hydrogen-ion concentrations at the different soil-water ratios. In order to study the influence of the solid phase on the reaction the writers conducted the following experiment.

The object of the experiment was to determine the effect of different amounts of the solid phase on inversion under conditions where the soil-water ratio would have little or no effect on the hydrogen-ion concentration. This was accomplished by using the displaced soil solution instead of water in making the suspensions. A large sample of acid soil was taken from a plot which has received sulfate of ammonia as a source of nitrogen for a number of years. The soil solution was displaced using the procedure of Burd and Martin (2). Sufficient sucrose was added to the displaced solution to make a 5 per cent sugar-soil solution. To 50-cc. portions of this sugar-soil solution were added different quantities of the soil, giving soil-solution ratios varying from 1 to 400 to 1 to 0.78. The suspensions were held at 79° to 81°C. for two hours, shaking by hand every fifteen minutes. After cooling the hydrogen-ion concentration, conductivity and invert sugar were determined. The results are shown in table 2.

An attempt was made to determine the hydrogen-ion concentration by the electrometric method. The results were unsatisfactory probably because of the high nitrate content of the solution and the consequent formation of ammonia at the hydrogen electrode. The reaction of the filtered extracts was then determined colorimetrically. All filtrates were apparently of the same hydrogen-concentration. Theoretically there should be no difference in the hydrogen-ion concentration of the suspensions since the displaced solution had been in equilibrium with the soil for several days when the soil-water ratio was approximately one to one-tenth. The results of the conductivity determinations indicate that the presence of the different amounts of soil had no effect on the composition of the solution.

TABLE 2

The sugar hydrolysis velocity constant, hydrogen-ion concentration, and specific resistance of soil suspensions having different soil-soil solution ratios

QUANTITY OF SOIL PER 100 CC. OF SOIL SOLUTION	HYDROGEN-ION CONCENTRATION	SPECIFIC RESISTANCE	SUGAR INVERTED	VELOCITY CONSTANT K
gm.	*pH*	*ohms*	*gm.*	
None	4.0	650	0.189	0.0003207
0.25	4.0	694	0.299	0.0005231
0.50	4.0	710	0.357	0.0006159
1.00	4.0	701	0.438	0.0008454
2.00	4.0	720	0.625	0.0011068
4.00	4.0	717	0.770	0.0013918
8.00	4.0	701	0.990	0.0018361
16.00	4.0	710	1.143	0.0021602
32.00	4.0	694	1.219	0.0023265
128.00	4.0	650	1.390	0.0027110

The results in table 2 show the influence of the solid phase on the rate of inversion of sugar when the hydrogen-ion concentration and conductivity were the same at all soil-solution ratios. It is evident that the solid phase exerts a considerable effect on the rate of inversion. As has been suggested (3, 7), this effect may be due to a concentration of hydrogen-ions at the surface of the soil particles. If there is a concentration at the surface of the particles it seems to depend on the acidity of the particles and might therefore be attributed to chemical forces. Such a hypothesis seems to satisfy many of the phenomena of soil acidity. However, additional investigations will be necessary to determine whether or not this conception of soil acidity is correct. Disregarding the question of the surface concentration of the hydrogen-ions, it seems evident that the rate of inversion is influenced by the acidity of the solid phase as well as by the acids that are in the soil solution.

SUMMARY

The strength of the acids in 25 soils was determined by the Truog avidity method, the sugar inversion method and by the hydrogen-ion concentration.

The last two methods were modified so that the same amount of acid was used in the determination for all soils. The results of the three methods correlate well and this is considered as an indication that the hydrogen-ion concentration of the soil solution is largely determined by the acidity of the acid silicates of the soil.

An experiment was made to determine the effect of the presence of different amounts of soil on the rate of sugar inversion when the specific resistance and hydrogen-ion concentration of the soil suspensions were constant. The presence of the acid soil greatly increased the rate of sugar hydrolysis. The explanation of the influence of the solid phase is not known. It may be due to a higher concentration of hydrogen-ions at the surface of the soil particles than in the solution.[2]

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[2] Additional studies on this problem, made since the manuscript was written, have led the authors to conclude that the explanation of the influence of the solid phase on sugar inversion is as follows: There is a higher concentration of hydrogen-ions at the surface and in the interior of the gel-like aggregates of soil colloids than in the free soil solution. This difference in the hydrogen-ion concentration is readily explained by Donnan's theory of membrane equilibria. The colloids of a mineral acid soil are complex hydrogen aluminum silicates. On hydrolysis these silicates give diffusible hydrogen-ions and non-diffusible silicate ions. According to Donnan's theory the presence of the non-diffusible ion causes an unequal distribution of the diffusible ions. In an acid soil suspension there would be a higher concentration of hydrogen-ions at the surface of the soil particles than in the free soil solution.

The application of Donnan's theory to the study of the system soil—soil solution is of the utmost importance. It is also important that it be considered in a study of the absorption of nutrient salts by plants. Jacques Loeb, "Proteins and the Theory of Colloidal Behavior," presents a clear explanation of Donnan's theory and gives experimental proof of its validity.